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Coordination and Reactivity in Organosilicon Compounds

A thesis presented for the degree of Doctor of Philosophy

by

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Department of Chemistry

The Open University

September 1991

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To my Motherland

Statement

The work embodied in this thesis was carried out by the author during the period of October 1988 to September 1991 in the Chemistry Department of the Open University under the supervision of Dr. A. R. Bassindale.

Part of this work has been published and is listed below:

- (a) "The interaction of nucleophiles with silanes; four, five and six-coordinate silicon compounds as models for intermediates in nucleophilic substitution at silicon" in the Ninth International Symposium on Organosilicon Chemistry, Edinburgh, 1990;
- (b) *J. Organomet. Chem.*, one paper in press.

Signed

Date

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I would specially like to thank my wife, Hui Xiu, for all reasons.

Abstract

The coordination chemistry of silicon in silane-nucleophile interactions is examined by solution NMR spectroscopy (^{29}Si , ^1H and ^{13}C) and conductivity measurements for acyclic, simple, multifunctional silanes $\text{R}_{4-n}\text{SiX}_n$ ($\text{R} = \text{Me, Ph, H}$; $\text{X} = \text{F, Cl, Br, I, OSO}_2\text{CF}_3$; $n = 2, 3, 4$) and a choice of nucleophiles ($\text{Nu} = \text{NMI, HMPA, DMAP, DMF, DMPU}$).

Coordination at silicon involves delicate balance between the steric and electronic effects of all the groups involved. Tetra-, penta- and hexa-coordinated silicon species, neutral or ionic, intermediates or final adducts, are all observed in solution, depending on the number and nature of the leaving and the R groups, the nature and quantities of the nucleophiles. No evidence of heptacoordination is found.

The ability to expand coordination at silicon increases with the increasing of the number of electronegative functional groups. The sequence of coordinate capability is SiX_4 , $\text{R}'\text{SiX}_3$ (hexa-) $>$ $\text{R}'_2\text{SiX}_2$ (penta-) $>$ $\text{R}'_3\text{SiX}$ (tetra-) when $\text{R}' = \text{Me, Ph}$. The nature of the leaving groups does not affect the maximum coordination number of the most stable adduct of a silane but determines the equilibrium constants K , which is in an order of $\text{I} > \text{OTf, Br} \gg \text{Cl} > \text{F} \gg \text{OR}''$ ($\text{R}'' = \text{Et, } i\text{Pr}$).

The H-containing silanes present a distinct example of the steric effect of the R groups. A replacement of R' by H often increases the maximum coordination number of the most stable silane-nucleophile adducts by one, together with an enhanced reactivity of the silane. The coordinate ability of H-containing silanes is in the order: HSiX_3 , $\text{R}'\text{HSiX}_2$, SiX_4 (hexa-) $>$ $\text{R}'_2\text{HSiX}$, $\text{R}'_2\text{SiX}_2$ (penta-) $>$ $\text{R}'_3\text{SiX}$ (tetra-).

The coordination at silicon is also determined by the steric hindrance resulting from the nucleophiles, which can be divided into two categories. Nucleophiles of group one

with smaller steric hindrance ($\text{Nu}^{\text{I}} = \text{NMI}, \text{DMAP}, \text{DMF}$) usually form silane- Nu^{I} complexes with coordination numbers greater by one than those of nucleophiles of group two with larger steric hindrance ($\text{Nu}^{\text{II}} = \text{HMPA}, \text{DMPU}$). The nucleophilicities of the nucleophiles only contribute to the equilibrium constant K .

The competitive processes between association and substitution in the interactions of silanes with nucleophiles result in the coordination at silicon changing with the quantities of the nucleophile presented. A number of reaction mechanisms are suggested. Some of the intermediate complexes are proved less reactive than their parent silanes or adducts to substitution.

Me_2HSiOTf and MeHSiOTf_2 are found to be effective reducing agents for aldehydes and ketones. They are the first simple silanes reported to be promising reducing agents without the presence of a catalyst. Factors affecting the reduction are discussed.

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Abbreviations

A acceptor or association

AO Atomic Orbital

br broad

DBPy 2,6-Di-tert-butylpyridine

Bipy 2,2-Bipyridine

δ chemical shift (in ppm)

d doublet

D donor or dissociation

DMAP 4-Dimethylaminopyridine

DMF N,N-Dimethylformamide

DMPU 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone
(N,N'-Dimethylpropyleneurea)

DNMR Dynamic Nuclear Magnetic Resonance

HMPA Hexamethylphosphoroamide (Hexamethylphosphoric Triamide)

HOMO Highest Occupied Molecular Orbital

J Coupling constant (in Hz)

K equilibrium constant

l large

LUMO Lowest Unoccupied Molecular Orbital

Me Methyl group

mmol. millimole

MO Molecular Orbital

mt multiplet

NMI N-Methylimidazole (1-methylimidazole)

NMR (n.m.r.) Nuclear Magnetic Resonance

n.r. not recorded

Nu Nucleophile

OTf Trifluoromethanesulphonate (triflate), CF_3SO_3

Ph Phenyl

q quartet

qu quintet

r molar ratio

R Alkyl or Aryl group

RP (or **SP**) Rectangular (or Square) Pyramidal

s small

sbr slightly broadened

sh sharp

t triplet

TBP Trigonal Bipyramidal

TMS Tetramethylsilane

vbr very broad

vs very small

vsh very sharp

X Halogen or OTf group or other functional group

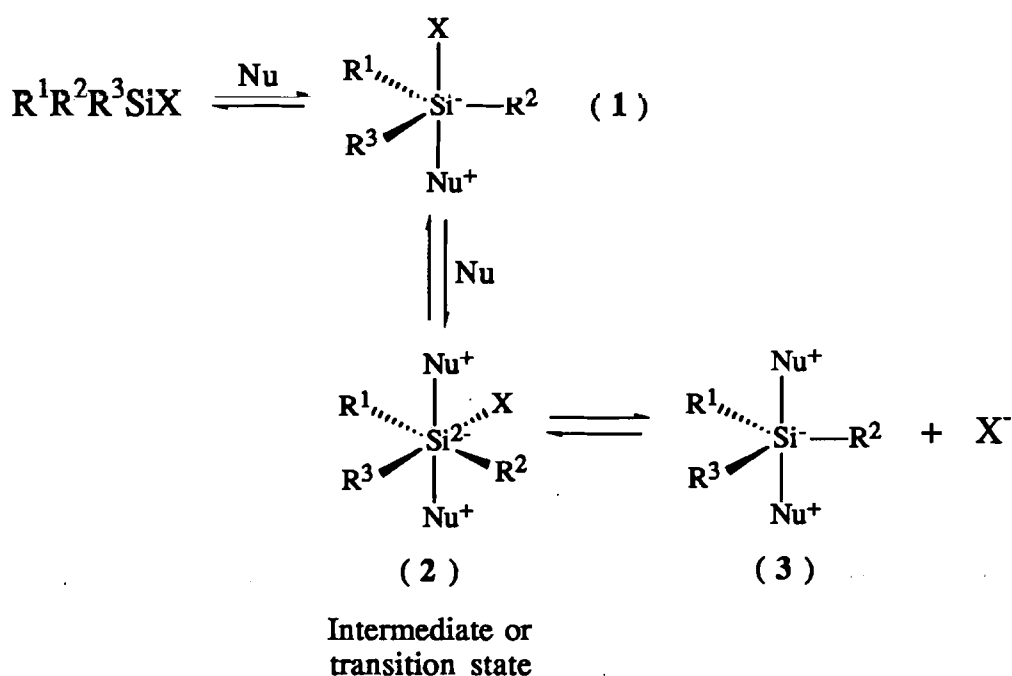
Chapter 1 Introduction

1.1 Introduction

Organosilicon compounds are increasingly in demand, both commercially and academically. However, the natural sources of silicon compounds are silica and silicates, which contain only Si-O bonds and are not practically useful for direct applications. Much work has been carried out on the synthesis of simple silanes, which can be further functionalized for specific uses. The Rochow direct process, discovered in the 1940s, revolutionized silicon chemistry making organosilicon compounds readily available in quantity¹. Since then the number and complexes of organosilicon compounds have both increased massively. Despite this, there is still much to learn about the chemistry of simple, small silanes.

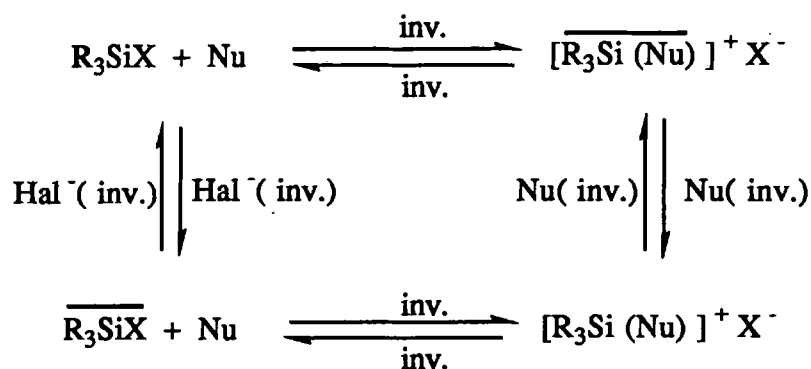
The mechanisms of reaction involving silicon have proved to be a most fruitful area of research for over forty years. Silicon engaging in nucleophilic reactions covers most of the known reaction mechanisms in solution. The nucleophilic substitution is of great importance in industry in the hydrolysis reaction of functional silicon compounds to produce silicones². Academically, the interest arises from the question of the nature of

the intermediates and / or transition states in hydrolysis reactions, the stereochemical outcome of reactions of chiral silanes and the possibility of forming hypercoordinate adducts. It was Sommer³ who first observed that optically active chlorosilanes were not optically stable in some solvents (acetonitrile, nitromethane, nitrobenzene). In studying the nucleophilically-activated racemisation and solvolysis of halosilanes, three mechanisms have been proposed. The one Corriu⁴ suggested involves expansion of coordination at silicon, forming a hexacoordinated intermediate (or transition state) during the rate-determining step (Scheme 1.1).

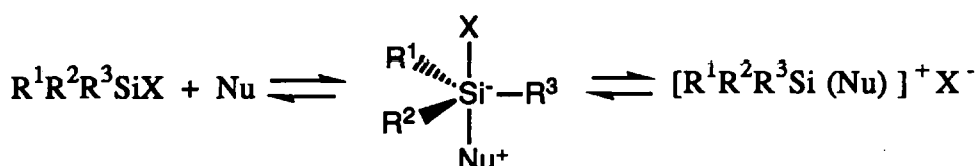


Scheme 1.1 The Corriu scheme.

Another one proposed by Chojnowski⁵ involves tetracoordinate ionic silicon species with ionization of Si-halogen bonds, and this has been expanded by the previous work of our laboratory⁶ to include halide exchange as shown in Scheme 1.2. Recently, Kummer⁷ proposed a pathway involving either coordination or ionization of Si-halogen bonds as a consequence of coordination (Scheme 1.3). The Kummer scheme is really a combination of the two limiting mechanisms.



Scheme 1.2 The Chojnowski-Bassindale scheme.



Scheme 1.3 The Kummer scheme.

However, in spite of many studies in this field no firm conclusions or general principles have been evolved. Moreover, most of the studies involved only monofunctional silanes $\text{R}_1\text{R}_2\text{R}_3\text{SiX}$, with mainly chelating agents. It is well known that the ability to form extra-coordination for silicon is closely related to the electronegativity of the surrounding groups and the configuration. The mechanism of nucleophilic substitution concerning multifunctional silanes is far from determined. Therefore one of the aims of this study is to throw light on the nature of nucleophilic reaction of multifunctional silanes by investigating the reactions between the silanes $\text{R}_{4-n}\text{SiX}_n$ ($\text{R} = \text{Me, Ph, H}$; $\text{X} = \text{F, Cl, Br, I, OTf}$; $n = 2, 3, 4$) and nucleophiles, such as NMI, HMPA, DMF, DMAP and DMPU in solution. Part I of this thesis is to deal with these reactions by examining the formation and stability of the adducts or intermediates, and the coordination numbers at silicon in these reactions, with which the mechanisms of nucleophilic reactions of multifunctional silanes are to be proposed and compared.

On the other hand, many reactions of silicon reagents may be classified as reductions. The addition of the Si-H linkage to multiply-bonded substituents can be brought about under catalytic or “ionic” conditions⁸. Recently the reactivity enhancement of hypervalent species of silicon has been explored and proved to be an increasingly interesting field⁹. In Part II of this study, the reactions between functional silanes $\text{Me}_{3-m}\text{HSiX}_m$ ($\text{X} = \text{OTf}$; $m = 1, 2$) and functional hydrocarbons are to be examined. The reduction of certain $\text{R}^1\text{R}^2\text{C}=\text{O}$ ($\text{R}^1 = \text{Me, Ph}$; $\text{R}^2 = \text{Me, Ph, H, NMe}_2, \text{OH, OEt}$) with $\text{Me}_{3-m}\text{HSiOTf}_m$ gives a new routine to organic syntheses.

Multinuclear NMR was chosen as the method of study, since the technique gives a ready availability to structural information¹⁰. In particular Silicon-29 NMR is a widely used, very sensitive probe¹¹, giving easy access to otherwise obscure information such as the coordination number of silicon. Furthermore it is also of considerable value for investigating the dynamic processes occurring in nucleophile / silane mixtures. Its use in conjunction with ^1H and ^{13}C NMR provides an extremely powerful tool for studying the intimate changes in the reacting molecules.

1.2 Particulars of the coordination chemistry of silicon

It is well known that organic silicon chemistry is related to but different from organic carbon chemistry. One of the major distinct characters is reflected by the easiness of silicon to expand its coordination. Generally speaking, all the differences come from the basic properties of both silicon and carbon at the atomic level.

1.2.1 Properties of silicon and carbon

The majority of silicon compounds in use today are carbon functional, and both carbon and silicon are in group IVA of the periodic table of the elements. Therefore a comparison of the chemistry of silicon and carbon is useful to fully comprehend and hence to predict the behaviour of organosilicon compounds.

A number of parallels can be drawn between the behaviour of the two elements, both of them normally have the tetrahedral geometry, for instance. Nonetheless, significant differences can also be easy to find¹². A remarkable example of the difference is the hydrolysis of the tetrachlorides of carbon and silicon. Silicon tetrachloride reacts violently with water while the carbon analogue is practically inert to hydrolysis. This is not just an isolated example. As a matter of fact, silicon compounds generally exhibit a much higher susceptibility towards nucleophilic attack¹². This dual role is responsible, at least in part, for the extensive and increasingly popular use of silicon in organic synthesis¹³ and practical applications.

In terms of atomic structure and properties, the main differences between carbon and silicon may be outlined as the following (Table 1.1):

Table 1.1 Some differences in fundamental properties of C and Si atoms.

	C	Si
Atomic number	6	14
Ground electronic configuration	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^6 3s^2 3p^2$
Radii of principal maxima of outer orbitals, pm ¹⁴	62.0 (2s) 59.6 (2p)	90.4 (3s) 106.8 (3p)
Atomic radius, pm ¹⁵	70	110
Covalent radius, pm ¹⁷	71.2	116.9
Ionization energies, eV, E_1 ¹⁸	11.26	8.15
Electron affinity, eV ¹⁹	1.12	1.39
Electronegativity, Pauling ^{20, 21}	2.5	1.8
Van der Waals radius, pm, Pauling ²²	170	217

(i) The covalent radius of silicon atom is one and one half that of the carbon atom, thus rendering the silicon atom more sterically accessible and able to be attacked in a more facile manner.

In nucleophilic substitution at carbon the bond to the leaving group must be broken, at least partially, before the nucleophile can enter. In the case of silicon, the reduced steric hindrance and strain due to the large size of silicon make it easy for a nucleophile to attack whilst the leaving group is still strongly bonded. The larger covalent radius helps to stabilize extra covalency at silicon and therefore contributes to reactivity by lowering activation energies.

(ii) The positive charge of the nucleus of silicon is shielded with an additional shell of 8 electrons and the electronegativity of silicon is lower than that of carbon.

Although Ebsworth²³ questioned the classical concept of electronegativity, it is nevertheless useful as a qualitative tool for rationalising trends. The low electronegativity of silicon, which remains relatively consistent whichever scale is chosen, results in polarisation of the $\text{Si}^{\delta+}\text{-C}^{\delta-}$ bond, even $\text{Si}^{\delta+}\text{-H}^{\delta-}$ as the Pauling electronegativity of H is larger (2.1)²⁴ than that of silicon as well. In this way silicon has an enhanced susceptibility towards nucleophilic attack, though other electronic factors such as the presence of electron donating (+I) substituents on silicon may offset this effect.

(iii) In contrast to the carbon atom, which does not have d-orbitals, the outer valence shell of silicon has vacant 3d atomic orbitals; In addition, silicon atoms have a higher electron affinity than carbon atoms (by 0.27 eV) and a greater ability to coordinate.

Explanations of structure-reactivity concepts in organosilicon chemistry have frequently relied upon d-orbitals. This effect includes the often termed (p-d) π interaction or d- π conjugation and the expansion of coordination at silicon. The fact that the distances for silicon bonded to elements with electronegativity values greater than carbon tend to be shorter than expected¹, that the bond angle widens with silyl ether²⁵,

and that silicon stabilizes alpha carbanions and beta carbocations^{26, 27} are often interpreted by involving 3d orbitals^{8,28}. Kanyha *et al*²⁹ studied the extents of d-orbital contribution by silicon with multinuclear NMR spectroscopy and claimed some evidence for (p-d) π bonding. However, the importance of 3d orbitals has been challenged^{30, 31}. Pitt^{32a} preferred to employ the hyperconjugation or σ – σ^* conjugation hypothesis in explaining the electronic properties of organosilicon compounds. Hiberty^{32b} revealed that the difference between the SiH_5^- and CH_5^- did not derive from the hypervalency associated with d orbitals but rather from the ability of Si to utilize its σ^* (Si-H) for bonding. Shambayati *et al*³³ favoured an explanation of Si-O bonds that considers the detailed nature of the HOMO and incorporates concepts from Walsh diagrams. These are said to account for the structural and chemical observations in a comprehensive manner. Anyway the arguments remain, and will not be discussed in detail here.

As far as extra-coordinate compounds are concerned, those of silicon have overwhelmed, in numbers, those of carbon (of which only one compound, resembling the highly energetic $\text{S}_{\text{N}}2$ transition state, a pentacoordinate species has so far been isolated³⁴ apart from carboranes and some odd organometallics). In contrast, a large number of penta- and hexa-coordinate silicon complexes have been proposed, many of which have been fully characterised by X-ray crystallography³⁵. The facile acceptor ability of the tetravalent silicon atom is usually interpreted with the assumption that the bonding process involves not only s and p AOs but also 3d AOs localized within the valence shell³⁶. A well established example is demonstrated by the octahedral hexafluorosilicate ion SiF_6^{2-} , where silicon forms six $3\text{sp}^3\text{d}^2$ hybrid bonds with the fluorine atoms. However, once again, the contribution of d-orbitals is rather controversial^{37a}. Ebsworth²³ proposed that d-orbital participation was not essential for the expansion of coordination. Nonetheless it is stressed that both the hyperconjugation effect and d-orbital contribution have to be considered in interpreting any experimental outcomes.

The nature and involvement in reaction mechanisms of the hypervalent silicon will be discussed in the following sections.

(iv) Valence electrons of silicon are at a much greater distance from the nucleus than in the carbon atom, as a result of which the polarizability of silicon is greatly facilitated; consequently silicon has a higher diffusion of its electron cloud and the ionization is about 3.1 eV less than that of carbon.

Compared with their carbon analogues, silicon forms markedly stronger single bonds with electronegative elements (oxygen, fluorine, chlorine etc.)³⁸, see Table 1.2.

Table 1.2 Dissociation energies of Si-X bond*.

Bond	Dissociation energy kJ mol. ⁻¹	Bond	Dissociation energy kJ mol. ⁻¹
Si-H	361~419	Si-F	628~694
Si-C	368~376	Si-Cl	449~472
Si-N	390~434	Si-Br	368~402
Si-O	477~549	Si-I	276~321

* In most cases, different values of dissociation energy were obtained for the same Si-X bond or in different compounds by various authors, see references 37b and 38.

In fact the Si-F bond is one of the strongest bonds known. Structural studies³⁹ suggested Si-F bonds are highly ionic and (p-d) π bonding plays no important role. Recent *ab initio* calculations⁴⁰ indicated that bonds between silicon and common nonmetals (H, C, O and F) are extensively polarized in the fashion (+)Si-X(-) to give significant charge transfers (0.65 ~ 0.92e). The ionic nature of these bonds allows silicon to be readily nucleophilically attacked and to expand its coordinate

sphere to form stable extracoordinate species, whereas carbon, has little such tendency. This helps to explain that the Si-X bonds, considering their rather high strengths, may be cleaved relatively easily, Si-F bond is comparatively inert to hydrolysis though.

On the whole, it is the fundamental similarities and differences of the two atoms that make silicon chemistry so interesting in both academic and application areas, though a universal theoretical interpretation is not available yet⁴¹.

1.2.2 Coordination chemistry of silicon

It is well known that all naturally occurring compounds and common products of silicon are present in a tetra-covalent state. However, the coordination chemistry of silicon has become more and more fascinating in the past decade. Numerous intensive investigations have been carried out concerning unusual degrees of coordination of silicon including those less than four coordination, multiple bonds, extra-coordination as well as tetracoordination^{1, 35}. The intention of this work is to study the involvement of coordination at silicon in the mechanisms of nucleophilic reactions of multifunctional silanes in solution and thus those with coordination number less than four will not be discussed here.

(I) Theoretical concept of hypercoordination at silicon

An understanding of tetra-coordinate silicon has been well established^{41, 42}. It is also known that the tetracoordinate silicon has an electron-acceptor ability to increase the coordination number to five, six and possibly even seven. However the nature of the electron-acceptor ability and its role in the hyper-coordinate state are still open to question.

In the widest sense of donor-acceptor interactions, silicon can use its five vacant 3d AOs to accommodate the incoming donors and then lead to hypercoordinate states. The participation of d AOs is generally considered in a hybridization fashion such as

sp^3d in a pentacoordinate species [$3d_{(z^2)}$ AO for TBP and $3d_{(x^2-y^2)}$ AO for RP]⁴³. In octahedral silicon complexes, two AOs [$d_{(z^2)}$ and $d_{(x^2-y^2)}$] participate simultaneously in the σ -bonding (sp^3d^2). The d_{xy} , d_{yz} and d_{xz} orbitals can be used for π -bonding with appropriate orbitals of the substituents⁴⁴. There are, of course, some other descriptions of extracoordinate silicon that do not include d orbitals. As one alternative, an electron-rich (four electrons) three-centre bonding model was proposed⁴⁶. Taking SiF_5^- for an example, the bonding molecular fragment along the F-Si-F axis is formed by the in-phase overlap of the central atom's p_z orbital and a p-orbital from each fluorine. With four valence electrons available, two occupy the bonding three-centre MO and two the approximately nonbonding MO. Thus, as found from experimental data, the three-center four-electron axial Si-F bond is of lower order of magnitude than the covalent two-electron bond. This so called " hypervalent bonding " is readily extended to induce hexacoordinate silicon complexes. In this way the electron density shifts from the central silicon atom to the bond and consequently the positive charge on silicon and the negative charge on fluorine are both increased. The rules of this bonding can be further stated as follows³⁵:

- a) The bond can be formed when ligands are more electronegative than the central silicon atom;
- b) The most electronegative substituents tend to occupy the axial position in a TBP molecule;
- c) The Si-X bond length is longer than that in a similar tetrahedral molecule;
- d) The bond decreases the electron density on the central silicon upon complexation.

It is worth noting that hypermetallic bonding (two-electron multi-center bonding) may also be possible to be involved in the expansion of coordination of silicon⁴⁷. All these schemes do not exclude other models⁴⁸.

(II) Formation of coordinated silicon complexes

It is commonly accepted that for silicon to exhibit complex formation ability it must have at least one electronegative substituent. There are only two exceptions reported

to date that the penta- and hexacoordinate complexes **4** and **5** (see Figure 1.1)

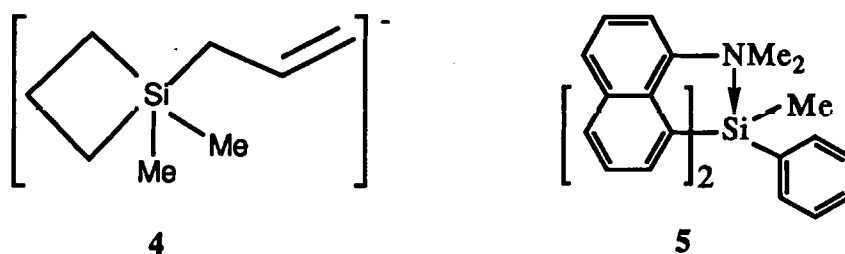
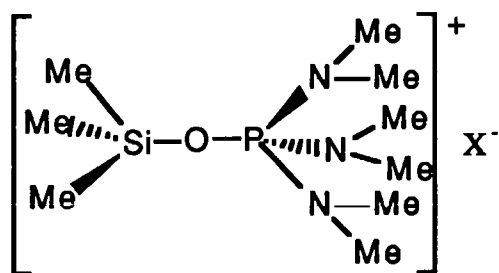


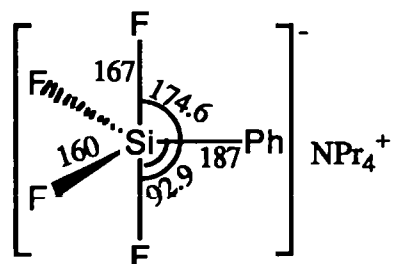
Figure 1.1 Hypercoordinate silicon complexes.

formed with four carbon substituents^{49, 50}. **4** exists in the gaseous phase when the allyl anion is added to 1,1-dimethylsilacyclobutane. However the formation of **5** is not so convincing. It is a very rigid and much crowded structure. The N atom in such a geometry is bound to be not far away from the Si atom and thus ¹H NMR spectra may be temperature-dependent. Therefore it remains critical for silanes to be functionalized in order to form complexes in solution. However the relationship between the complex formation and the degree of functionalization of a silane is still not certain. Within those reported identified stable complexes, much depends on the donor.

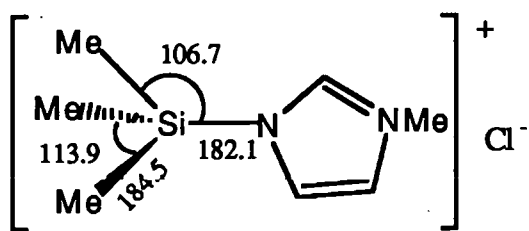
The effect of ligand geometry on the coordinate ability of silicon compounds is diverse and can only be evaluated qualitatively. The simplest model is the complexes formed in the reactions between functional silanes and monodentate nucleophiles to give acyclic products. Species such as [R₃Si(Nu)]⁺ X⁻ have been postulated for a wide variety of nucleophile-silane combinations. For the mono-functional silanes, Chojnowski⁵ isolated and characterised 1:1 adducts **6** between Me₃SiX (X = I, Br) and HMPA. Bassindale and Stout^{51a} claimed the donor strength of nucleophiles measured by Beta (Taft) is correlated with the ²⁹Si chemical shift of the [Me₃Si(Nu)]⁺ X⁻ (X = Cl, Br, I, OTf, ClO₄, NMI) complexes and the relative magnitude of the equilibrium constant for adduct formation. Hensen^{52a} subsequently actually crystalized and X-ray analyzed [Me₃Si(NMI)]⁺ Cl⁻ (**7**). It is noticeable that



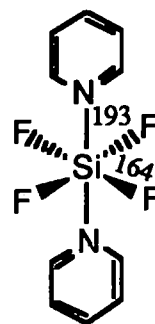
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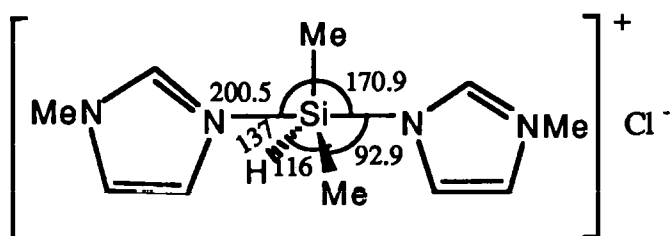
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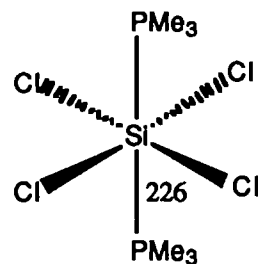
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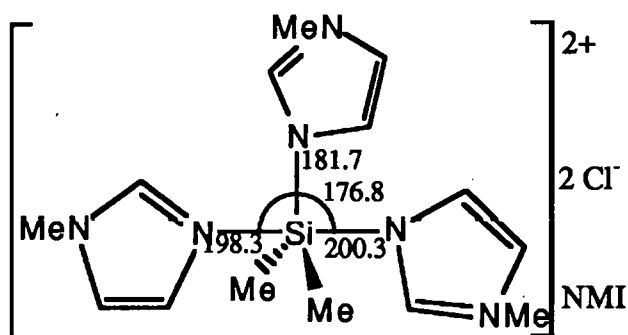
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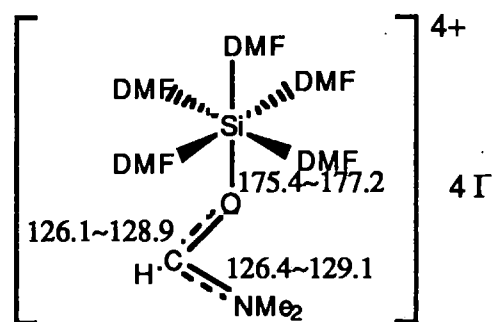
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12



9



13

Figure 1.2 Structures of some coordinated complexes.

the replacement of an alkyl group with hydrogen seems to increase the coordinate ability at silicon. Lau⁵³ showed that four coordinate ionic salts $[\text{PhMeHSi}(\text{Nu})]^+ \text{Cl}^-$ undergo second nucleophilic attack yielding stable penta-coordinate ionic adducts $[\text{PhMeHSi}(\text{Nu})_2]^+ \text{Cl}^-$. X-ray crystallographic analysis revealed^{52a} both Me_2HSiCl and Me_2SiCl_2 forms stable pentacoordinate complexes with NMI (see 8 and 9).

There is a strong link between the number of functional groups surrounding a silicon and the ability of the silicon to increase its coordination number, but no detailed direct literature is available yet. It is clear that the more electronegative substituents a silane has, the easier it is to form higher coordinate complexes. Compounds such as **10**⁵⁴, **11**⁵⁵, **12**⁵⁷, **13**⁵⁷ have been identified. The structural details of such adducts have much to do with the properties of the leaving groups and the nucleophiles. The Si-F and Si-Cl bonds in **11** and **12**, for instance, tend to remain when the coordination number increased whereas the Si-I bonds in **13** have been totally replaced. In addition, SiI_4 forms 1:6 complex with NMI and 1:4 with Py but no adduct with isoxazole; the 1:4 complex is easily hydrolyzed whereas the N-hexacoordinated one is resistant to solvolysis⁵⁸. On the other hand, $\text{Si}(\text{OMe})_4$ displays little tendency to form complexes, although $\text{Si}(\text{OR})_5^-$ (R = Me, Et, n-Pr, i-Pr, CH_2CF_3 and p-Mc- C_6H_4) is reported^{60h}.

The largest part of the body of hyper-coordinate complexes of silanes result from endocyclic and chelate reactions. The ring formation always enhances the stability of the complexes, *eg.* the intramolecular reaction favours expansion of the coordinate number. For example, bis (ethylene-1,2-dihydroxy) silane forms a pentacoordinate adduct readily with alkali metal alkoxide **14**^{60a}, which is not easily observed for the acyclic silicon analog $\text{Si}(\text{OCH}_3)_4$. The stabilization of TBP compounds of silicon relative to the corresponding four-coordinate tetrahedral species by bridging of an apical and an equatorial position with five-membered rings such as **15** has been well documented⁶¹. The equatorial electropositive ligand bonded to the central atom in five-membered rings enhances the difference in electronegativity between the central atom and the apical ligand, and leads to a stable hypervalent bond. The fact that the cyclic ligand has a smaller configuration entropy and is ready for complex formation

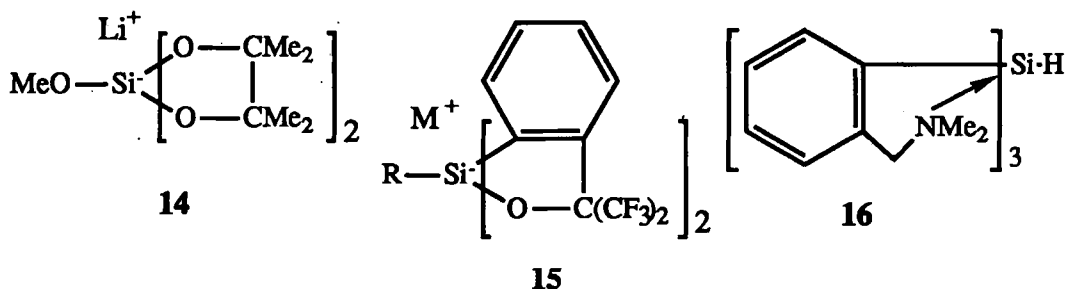
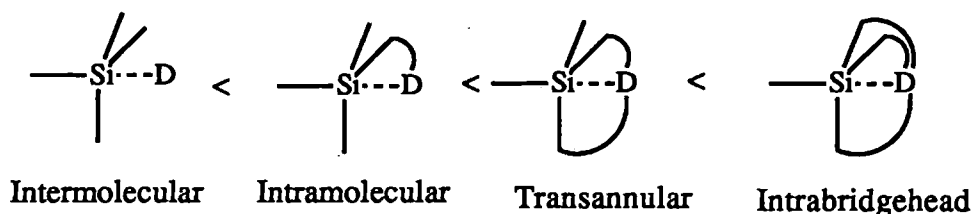


Figure 1.3 Intramolecular coordinated silicon complexes.

produces an extra entropy and enthalpy stabilization⁶². A five-membered saturated ring has the strongest such chelate effect⁶³. The more rings a silane has, the more stable a higher coordinate complex will be. Tandura³⁵ suggested that the stability of the complexes increases in the following sequence:



Scheme 1.4 Ease of forming intramolecular coordination.

There are assumptions of possible hepta- and octa-coordination of anionic complexes of silicon, although there are considerable doubts about them^{35,64}. However, Corriu⁶⁵ claimed that the reaction of HSiCl_3 and 2-((dimethylamino)methyl) phenyllithium would produce a neutral seven-coordinate complex (16) like that of germanium though no direct detailed data are available yet.

The extent of coordination of coordinated compounds can vary with a change of the state of aggregation⁶⁶. The strength of D-A bonds increases when passing from the gaseous to solution and then to the crystalline state, and with decreasing temperature and increasing pressure.⁶⁷ In solution, the nature of the solvents as well as their

extent of aggregation, affects considerably intermolecular interaction⁵¹. In this case, factors affecting chemical equilibrium should all be considered.

(III) Structure of silicon complexes

Coordinated silicon compounds can be divided into neutral compounds and ionic (anionic or cationic) complexes. As far as the stereochemical arrangement is concerned, there is not much difference within the compounds which have the same coordination number⁴².

It is generally accepted that four-coordinate silicon compounds are tetrahedral. However, the bond angles of silicon in such compounds are more readily distorted than the corresponding bond angles of carbon in isostructural analogs⁶⁸. The four-coordinate salt compounds such as **7** and $[\text{Me}_3\text{Si}(\text{py})]^+ \text{X}^-$ ($\text{X} = \text{Br}, \text{Cl}$)⁶⁹ have been proved to be slightly distorted tetrahedra.

For the five-coordinate silicon compounds, from a geometrical point of view, it is impossible to place five points in equivalent position on a spherical surface excepting a planar arrangement. There are two types of favoured structures, the trigonal bipyramid (TBP) with D_{3h} symmetry and the square (or tetragonal) pyramid (SP) with C_{4v} symmetry, see Figure 1.5.

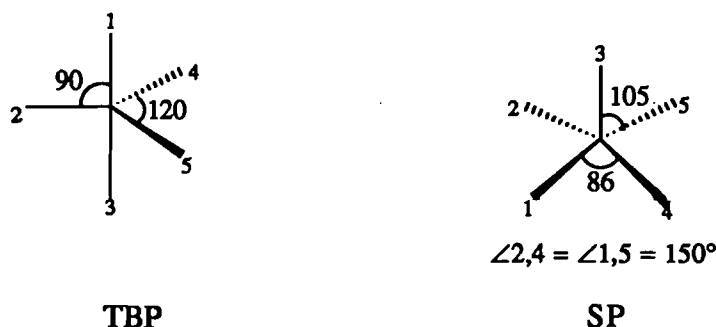


Figure 1.5 The favourable structures of pentacoordinate compounds.

The minimum repulsive valence shell interactions between five identical ligands around

the central silicon atom corresponds to TBP in which two axial bonds are longer than three equatorial bonds⁷⁰. Acyclic pentacoordinate main group elements, including silicon, take this arrangement, which is more stable than SP and the most electronegative substituents occupy the axial position. For the TBP molecules of the $\text{SiX}_{5-n}\text{D}_n$ type there are six possible achiral isomers as shown in Figure 1.6.

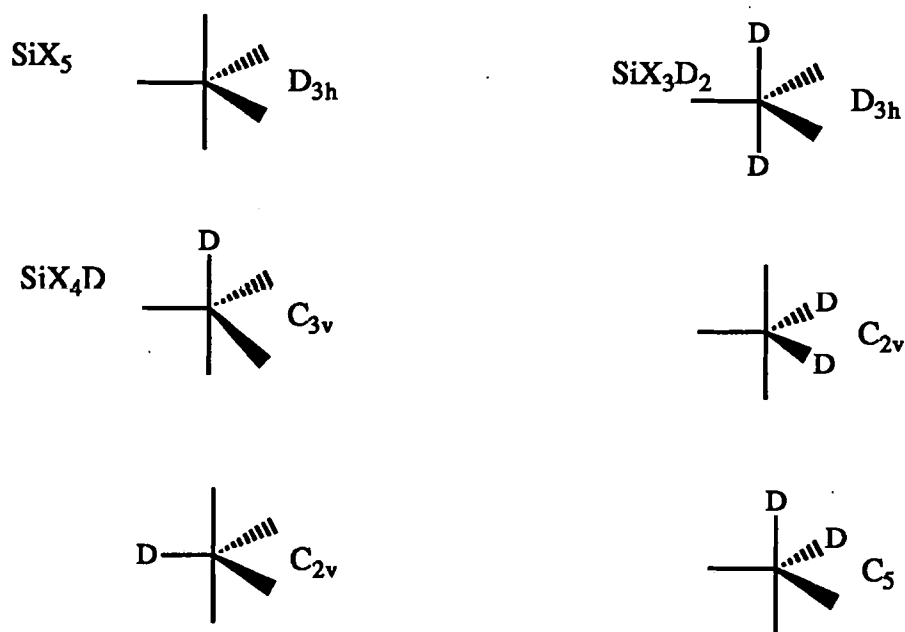
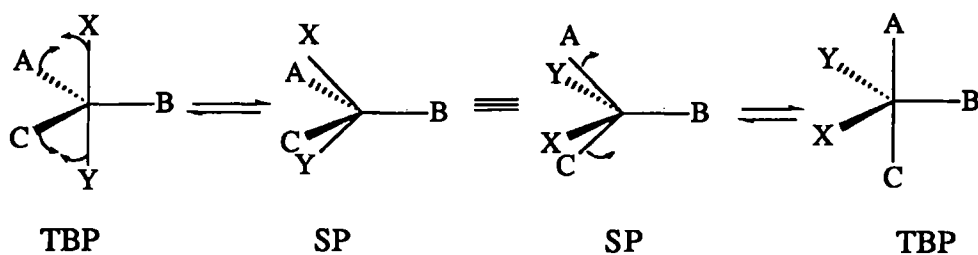


Figure 1.6 Possible symmetries for $\text{SiX}_{5-n}\text{D}_n$.

The presence of two unsaturated five-membered rings in spirocyclic derivatives is a general principle in forming SP for most pentacoordinate main group elements as well as silicon⁷¹. A slight “bond-bending” of TBP can lead to SP and it is not difficult to perform. For example, all fluorine atom in SiF_5^- at a temperature down to -66°C are spectroscopically equivalent^{54b}, which indicates intramolecular exchange processes. There are a number of mechanisms proposed for intramolecular rearrangements in pentacoordinate complexes⁷², in which the Berry pseudorotation^{73a} is most widely accepted, as is shown in scheme 1.5. In the process one equatorial position (B), called the pivot ligand, is fixed while the two others are exchanged with the two axial position. A series of geometries ranging from TBP to SP of pentacoordinated silicon



Scheme 1.5 Berry pseudorotation.

compounds have been observed by X-ray analysis^{73b}. Recent *ab initio* and semiempirical calculations^{73c} on SiH_5^- confirmed the Berry pseudorotation of silane and predicted the barriers to be about $2.4 \text{ Kcal mol}^{-1}$.

For the six-coordinate species, they are always octahedral. In the case of SiX_4D_2 complexes, unlike SiX_6 (O_h) and SiX_5D (C_{4v}), there are two possible isomers: trans (D_{4h}) and cis (C_{2v})³⁵. For the acyclic ones, the D ligands usually occupy the trans position though in some cases geometrical factors can cause cis orientation of the ligands (for instance F_4SiBipy ⁷⁴). Quantum chemical calculations have shown⁷⁵ that the structure could be affected by (p- π)d bonds, and electrostatic interactions in addition to spacial requirements.

1.3 Coordination and nucleophilic reaction mechanisms in silicon compounds

The stereochemistry and mechanisms of nucleophilic attack at silicon are increasingly attracting attention. Based on the pioneering work of Sommer³, Corriu⁷⁶ has shown the picture to differ from that of carbon and to resemble that of phosphorus. There are several mechanisms and reviews provided by various authors^{4, 5, 6, 7, 38, 77, 78, 83}. The major discrepancies between those proposed mechanisms lie mainly with the interpretation of the reaction pathways which concern the nature and coordination of the transition state and intermediates. The following is only a brief summary of the

story and the mechanisms of reactions of highly hindered organosilicon compounds are excluded.

1.3.1 Factors affecting the outcome of nucleophilic reactions of silanes and their interpretations

The mechanism study of nucleophilic substitution at silicon is related to its stereoselectivity, either retention or inversion, which depends on the silane itself, the leaving group, the nucleophile and the medium in solution. In fact, these factors govern the kinetic behaviour of the nucleophilic reaction of silanes as well.

(I) Nature of the silane

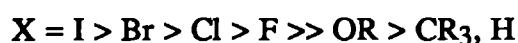
The reactivity of a silane is delicately balanced between the steric and electronic effects of the substituents. The rate of hydrolysis and alcoholysis of chlorosilanes increases with the number of chlorine atoms bonded to silicon^{80a}. In the alkyl series of methyl, ethyl, *i*-propyl and *t*-butyl, a very large decrease in the rate of substitution is observed. Increasing the electron donating ability of an aryl substituent on silicon, in order to stabilize the siliconium ion if S_N1 operates, slows down nucleophilic substitution^{80b}. It is worth noting here that the reason why S_N1 is ruled out in nucleophilic substitution at silicon in solution is not that the siliconium ion is difficult to form but that the counter ions normally used to stabilize carbonium ions are excellent nucleophiles for silicon and these anions cannot be used to slow down the faster S_N2 -Si Reaction^{38, 80c}. Cartledge⁸¹ applied steric parameters, derived from the reactivities of carbonyl compounds, to the reaction at silicon and established a set of parameters for the silicon and showed that steric effects in $R_1R_2R_3SiX$ compounds are often additive.

Sommer^{3b} suggested that the stereochemical outcome of the substitution had little to do with the structure of the alkyl or aryl groups on the silicon. There is, however, a significant change when a silicon atom is made part of a strained-ring structure⁷⁸. The angle strain of the ring at silicon favours retention if the leaving group is exocyclic and

inversion if the leaving group is endocyclic. The interpretation of the change can refer to a stronger apicophilicity of small rings or a frontier orbital interaction and will not be further discussed.

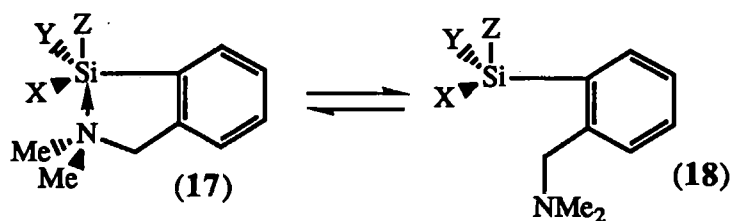
(II) The leaving group (LG)

The reactivity of silanes with different leaving groups, *eg.* R_3SiX , towards nucleophiles decreases in the order:



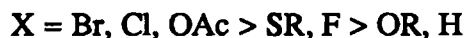
In view of the stereochemical outcome, it was pointed out by Sommer that good leaving groups with low basicity ($pK_a < 6$, *eg.* Br and Cl) tend to give inversion of configuration while poor leaving groups of high basicity ($pK_a > 10$, *eg.* H and RO) favour retention of configuration^{3b}. The tendency of halosilanes to undergo racemization and the preference for inversion over retention of stereochemistry upon nucleophilic attack at silicon both follow the same trend as that of the relative ability of the leaving groups to be displaced⁸². The bond polarization and the Si-X bond stretching during attack by the nucleophile have also been considered of importance⁸³. Nevertheless, the explanations of the stereochemistry of nucleophilic displacement at silicon with basicity, electronegativity and bond polarizability and stretching of the leaving group fail to account for all cases satisfactorily.

Corriu⁸² carried out an extensive NMR study on the system shown in Scheme 1.6 and suggested that an intramolecular Si-N bond formed, leading to an expansion of



Scheme 1.6 Equilibrium of intramolecular coordination.

coordination at silicon. Using variable temperature ^1H and ^{29}Si NMR, he assessed the relative ease of pentacoordinate formation in the following order:



It has been noted that the ease of expansion of coordination at silicon, the increasing rate of racemization as well as the increasing proportion of inversion of configuration all follow the the same order.

To further interpret the effect of the leaving group on silicon in the nucleophilic reaction of silanes, the concept of apicophilicity was introduced. It is defined as the change in energy when an apical and equatorial substituent exchange position in a TBP. Corriu^{82a} used variable temperature ^{19}F NMR, which can distinguish the apical and equatorial fluorine atoms by their different environment and enables the relative apicophilicity of various substituents to be determined. He found that a fluorine substituent in the derivatives of $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{SiXYZ}$ (Scheme 6, $\text{Y} = \text{Me}$, $\text{Z} = \text{F}$) was apical when $\text{X} = \text{H}$, OR or NR_2 but equatorial for $\text{X} = \text{Cl}$. A mixture of the two configurations was observed for $\text{X} = p\text{-YC}_6\text{H}_4\text{CO}_2$ ($\text{Y} = \text{H}$, OMe and NO_2), the $\text{F}_{\text{ax}} / \text{F}_{\text{eq}}$ ratio depended on the nature of the para-substituent Y . An experimental apicophilicity was given in the following order^{82b}:



The point of using the term apicophilicity is that it parallels leaving group ability, hence the ease of coordination expansion etc.. For acyclic derivatives having simple ligands, apicophilicity integrates a number of factors including electronegativity, inductive effects and π -bonding contributions. Small-ring strains are considered in cyclic compounds. A couple of *ab initio* calculations have supported this concept and agreed generally with the experimental order^{77, 84}.

(III) The attacking nucleophile

The reactivity and stereochemistry of silanes are also affected by the attacking

nucleophile. The previous work in our laboratory⁵¹ on the reaction of $R_1R_2R_3SiX$ and nucleophiles in solution showed 1:1 [Nucleophile-Silane]⁺ X⁻ adducts formed. The relative magnitude of the equilibrium constant for the adduct formation was correlated with Taft's Beta values, supporting Frye's kinetic results² for the alcoholysis of Ph_2SiCl_2 , and could be specified in the following order:



The fact that the stereochemical outcome varies as a function of the nucleophile for a range of leaving groups, and in which the dominant factor is the electronic character of the nucleophile, led Corriu^{82, 83} to relate the preference for retention with the hardness of the attacking nucleophile. Hard nucleophiles with localized negative charge such as CH_3CH_2Li give retention whereas soft nucleophiles with delocalized negative charge such as $PhCH_2Li$ lead to inversion. Anh and Minot⁸⁵ supported these ideas by calculation and proposed a frontier orbital interaction between the nucleophile's HOMO and the substrate's LUMO as shown in Figure 1.7. The size of the LUMO and

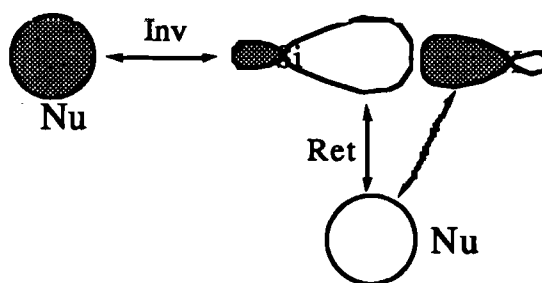


Figure 1.7 Frontier orbitals interaction in substitution at silicon.

HOMO orbitals are very sensitive to changes in the nature of the leaving group and the attacking nucleophile respectively and subsequently affect the outcome of the stereochemistry. A frontside attack, giving retention, corresponds to an attack on the large lobe on silicon, which is made easier compared to that of carbon due to the fact that Si-X bond is longer and more diffuse, but will be opposed by an unfavourable

out-of-phase overlap between the nucleophile and the leaving group. A backside attack with inversion corresponds to an attack on the small lobe on silicon without unfavourable interaction. A hard nucleophile is usually small, with contracted valence orbitals, so that the repulsion from a long-range overlap with the leaving group will be negligible and the frontside attack is favoured, leading to retention of configuration. A soft nucleophile, however, usually has diffuse valence orbitals and the unfavourable interaction will be large enough to prefer backside attack leading to inversion. Thus the stereochemistry depends on the balance between the favourable interaction of the nucleophile with the reaction centre and the unfavourable interaction of the nucleophile with the leaving group. It is also easy to understand that a reduction of the hardness of the nucleophile, implying a decreasing of the energy of HOMO and an increasing HOMO-substrate superjacent MO, favours inversion of configuration⁷⁸.

The concept of hard / soft nucleophile has also been applied to the formation of pentacoordinate intermediates upon reacting silanes. Corriu⁸³ proposed that an approach of a soft nucleophile at 180° with respect to the LG, corresponding to an axial entry, was favourable and led to inversion while an approach of a hard nucleophile at 90° with respect to the LG, corresponding to an equatorial entry, was preferable and implied a retention outcome. However, Holmes⁸⁴ argued by calculations that the equatorial entry and apical departure was a high-energy process and the axial entry and apical departure including a Berry pseudorotation was more favourable. He further suggested that a change of the hard / soft character of the nucleophile altered to a different extent of the overlap population of the LG in both axial and equatorial positions, subsequently affecting its apicophilicity. Softer nucleophiles increase the apicophilicity of the LG leading to inversion and harder nucleophiles decrease the apicophilicity of the LG favouring retention.

The general relationship among the various factors, concerning the LG and Nu, affecting the stereochemistry and reactivity of the nucleophilic substitution at silicon in solution can be outlined in the following scheme (Scheme 1.7):

	H < OR << F, SR << Cl < Br, OTf	
Stereochemistry:	Retention	Inversion
Hardness as nucleophile:	Hard	Soft
Apicophilicity:	=====→	
Ease of racemization:	=====→	
Ease of displacement:	=====→	
Ability to pentacoordinate:	=====→	

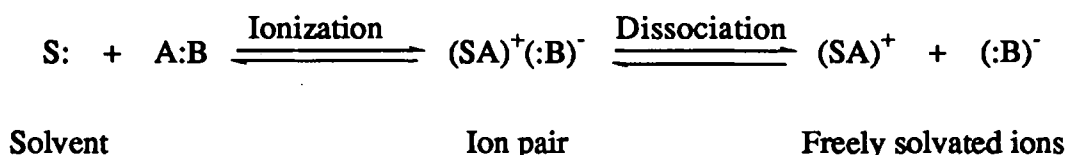
Scheme 1.7 Summary of the effects of LG and Nu.

(IV) The medium

The medium, including solvents and additives, plays a very important role in the nucleophilic reactions of silanes in solution. In the reaction between chlorosilanes and methanol, for instance, not only the reactivity can be increased but also the stereochemistry can be altered completely from inversion to retention by changing the solvent from non-polar ones such as carbon tetrachloride or hexane to polar ones such as HMPA or DMF. The influence of electrophilic assistance of the additives is reported obvious as well⁸³. It is necessary therefore to look into the properties of the solvent before going any further.

Two important properties of a solvent should be distinguished, namely, its donicity and its dielectric constant. The donicity of a solvent is a measurement of its Lewis base strength or its ability to behave as a nucleophile. The dielectric constant comes essentially from the dipole-dipole interactions within the solvent molecule and reflects the ability to solvate charged species, though the polarity or dipole moment is also an expression of assessment of the solvating potential of a solvent. The relative importance or balance between the donicity and dielectric constant depends upon the system under examination and determines the outcome of a reaction. For example, the formation of a pair of freely solvated ions from ionization of a covalent compound

occurs by two distinctive steps, as shown in Scheme 1.8. The first step (ionization



Scheme 1.8 Effects of solvent in solution.

or ion formation) depends largely on the nucleophilic property of the solvent and has little to do with the dielectric constant. However, the dielectric constant of the medium is the major factor in determining the degree of the dissociation of the ions in the second step. Thus the two properties together govern the concentration of the fully dissociated ions. Conductivity studies are usually used to determine the existence and the concentration of the ionic species. But the results from the measurement of the electric conductivity of the solution must be elucidated with great care. While a highly conducting solution must be composed of dissociated free ions, a non- or low conducting solution may consist of ion pairs or indeed no ions at all.

Corriu⁸³ found the nucleophilicity of a solvent became much more important than its ability to stabilize and solvate a charged intermediate in studying the racemization of chlorosilanes in solvents with very low dielectric constant but moderate donicity. Solvents act like nucleophiles in some cases. It is therefore necessary to take the two properties seriously in the nucleophilic reaction of silanes. Several attempts have been made to quantify solvent properties, no leading theory has been proved to be completely satisfactory yet though.

i) DN and AN scales: Gutmann⁸⁶ suggested that the ionization of a covalent compound was a coordination-chemical phenomenon and there were no principal differences between “weak” and “strong” coordinating interactions. He demonstrated that the ionization generally increases with increasing donor strength of the donor or

with increasing acceptor strength of the acceptor and hence proposed two parameters: a donor number or donicity (DN) in line with the nucleophilic property and an acceptor number (AN) according to the electrophilic character of the solvent. The donor number (DN) is defined as the negative ΔH in Kcal.mol^{-1} of the interaction of the electron pair donor (EPD) with SbCl_5 in a highly diluted solution of dichloroethane as expressed in Equation 1.1.

$$\text{DN} = -\Delta H_{\text{EPD-SbCl}_5} \quad \text{Equation 1.1}$$

The value of DN is therefore a reflection of the solvent- SbCl_5 strength while the entropy effects are assumed to be constant. The acceptor number (AN) is a dimensionless number derived from the ^{31}P NMR shifts produced where triethylphosphine oxide ($\text{Et}_3\text{P}=\text{O}$) dissolves in the chosen solvent, related to an arbitrary value of 100 for the $\text{Et}_3\text{PO-SbCl}_5$ adduct dissolved in 1,2-dichloroethane. Both DN and AN are the reference to substance for assessing the donicity.

ii) E and C scales: Drago and Wayland⁸⁷ suggested that the reaction enthalpy ΔH of an acid-base interaction was governed by two empirical and independent factors, namely, the electrostatic (or ionic) and covalent characters of the individual acids and bases involved. Accordingly they used a double scale equation (Equation 1.2)

$$-\Delta H = E_{\text{acid}} E_{\text{base}} + C_{\text{acid}} C_{\text{base}} \quad \text{Equation 1.2}$$

to correlate and predict enthalpies of the adduct formation in the gas phase and poorly solvating solvents. E shows the ability of the acid (acceptor) and base (donor) to participate in ionic bonding whereas C describes their ability in covalent bonding.

iii) Linear solvation energy relationships (LSER): Taft *et al.*⁸⁸ proposed that acids and bases could be defined as hydrogen-bond donors and hydrogen-bond acceptors

respectively. They developed a number of scales of solute or solvent properties which could be expressed by the generalized form as shown in Equation 1.3. The term XYZ in the equation is a measurable physical character such as a position or intensity or

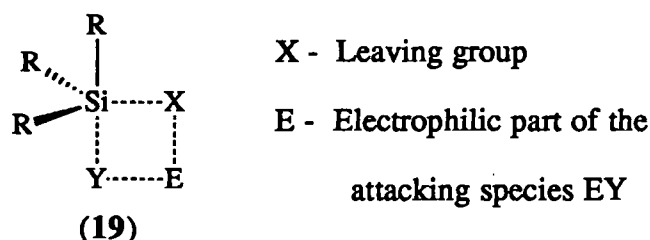
$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H + e\xi \quad \text{Equation 1.3}$$

maximal absorption in an NMR, ESR, IR, UV /visible constant etc.. By judicious choices of solvents and / or reactants or indicators followed by careful treatment of the data, they formulated the following parameters:

- (1) π^* , the scale of the index of solvent dipolarity / polarizability which measures the ability of the medium to stabilize a charge or a dipole by virtue of its dielectric effect.
- (2) δ , the “polarizability correction term” reflecting the differences in solvent polarizability (equals 0.0 for nonchlorinated aliphatic solvents).
- (3) α , the scale of HBD (hydrogen-bond donor) acidities describing the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond.
- (4) β , the scale of HBA (hydrogen-bond acceptor) basicities providing a measurement of the ability of the solvent to accept a proton (donate an electron pair) in a solvent-to-solute hydrogen bond.
- (5) δ_H , the Hildebrand solubility parameter related to the solute molar volume measuring the solvent-solvent interactions that are interrupted in creating a cavity for the solute.
- (6) ξ , the coordinate covalency measurement correlating the basicity properties of different functional groups.

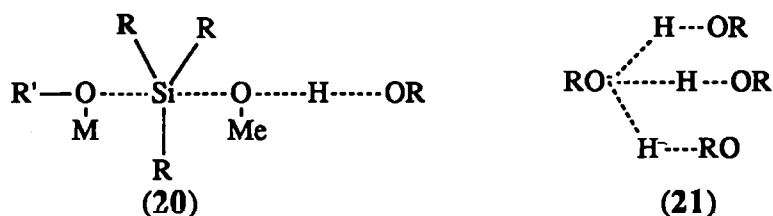
These parameters have provided a unified scales of various solvent effects and have been gaining popularity. The equilibrium constant of the reaction of nucleophiles reacting with monofunctional silanes, for example, has been proved to be in direct proportion to their β values⁵¹.

The effect of the medium on the nucleophilic reactions is no less complex and interesting. From calculation and stereochemical outcome, Sommer³ suggested that inversion occurs when a counteranion was able to assist the departure of the leaving group. For poor leaving groups, he proposed a four-membered cyclic mechanism (Scheme 1.9) involving electrophilic assistance from E (the electrophilic part of the



Scheme 1.9 S_Ni -Si mechanism

attacking reagent). This species (19) could be SP with X and Y basal resulting in both inversion and retention or TBP with Y apical and X equatorial producing retention outcome. Such electrophilic assistance can be further demonstrated in the dramatic movement from retention to inversion of configuration of the products in the substitution of alkoxy, mercapto and fluorosilanes with alkoxide ions as the percentage of alcohol in the benzene solution increases. Sommer³ believed that electrophilic assistance from the counteranions in the form of **19** was required in benzene to enable the leaving group to be expelled. Obviously the increasing hydrogen bond ability of the alcohol is able to promote inversion (see **20** in Scheme 1.10). It is noteworthy that a



Scheme 1.10 Solvent assistance involved in nucleophilic reactions.

transition state of expansion of coordination at the silicon atom is involved in both cases. However, these conclusions have been disputed by Corriu^{83, 84}, who explained the effects of the medium in terms of the hard /soft approach. He suggested that solvents changed the hardness /softness of the attacking nucleophiles and altered the stereochemistry accordingly, as is shown by **21** (Scheme 1.10) and that the negative charge of RO^- was delocalized by the hydrogen bonds of the alcohol resulting in a softer species that reacted with inversion. The distinctive stereochemical outcome of the organometallic nucleophiles such as RLi , RMgX and LiAlH_4 etc. and their behaviour in different medium can be rationalized similarly. Even for the difunctional silanes $\text{R}^1\text{R}^2\text{SiXY}$ ($\text{X}, \text{Y} = \text{F}, \text{OR}$ etc.) Corriu argued that soft reagents that led to inversion cleaved only the better leaving group, namely F, and the electrophilic assistance for hard reagents could only determine which group was to be cleaved without affecting the stereochemistry.

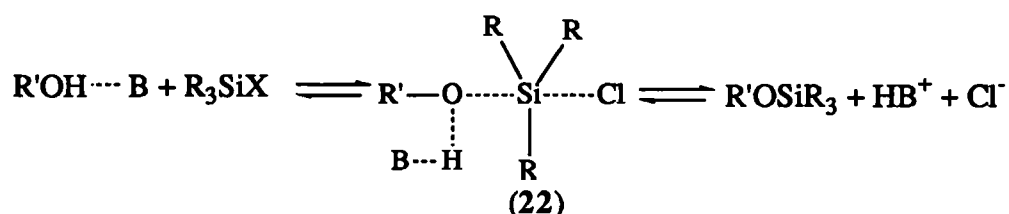
1.3.2 Coordination and pathways of nucleophilic reactions of silanes

The mechanisms of nucleophilic substitution at silicon have been studied on numerous occasions since Sommer's first report^{3a} in 1964. But the subject remains of active controversy. The most contentious aspect is the role of the extracoordinate silicon intermediates in such reaction, although the $\text{S}_{\text{N}}1$ pathway was normally ruled out because of the high stereochemical selectivity of the reaction and the strong sensitivity to nucleophiles of silanes. The representative work can be briefly summarized in the following four mechanistic viewpoints involving pentacoordination, pseudorotation, ionic species and further expansion of coordination.

(I) Involving pentacoordination

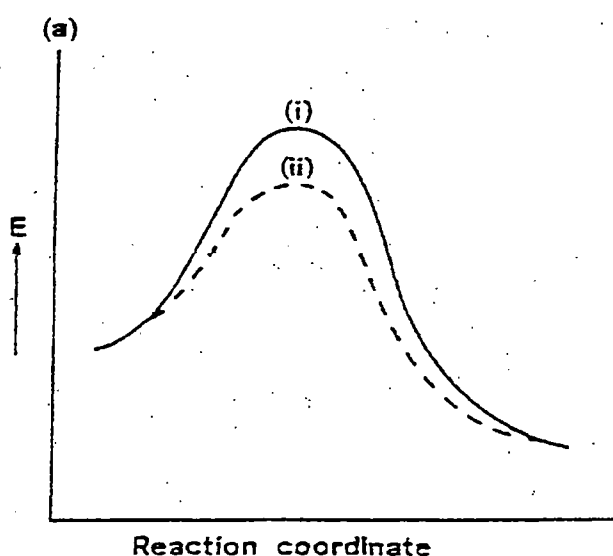
The fact that silicon compounds can form pentacoordinate complexes has been widely accepted. Sommer^{3b} proposed that the dominant mechanism leading to inversion at silicon was an $\text{S}_{\text{N}}2$ process resembling that observed at carbon. In the case of silicon, the process would involve a more stable (compared with carbon) pentacoordinate

transition state or intermediate, which is expressed as S_N2^* -Si and S_N2^{**} -Si, depending on the nature of the reaction under examination and the rate determining step. The energy profiles for these processes are shown in Figure 1.8, together with their corresponding rate laws. The inherent characters of silicon help to reduce the activation energy and to stabilize the pentacoordinated transition state / or intermediate. These processes become progressively more important as the silicon is surrounded with more electronegative groups, *eg.* $R_3SiX < R_2SX_2 < RSiX_3 < SiX_4$ (where X is a high electronegative group). Macharashvili *et al*^{73d} studied the X-ray structure of N-(halogenodimethylsilylmethyl)lactams and suggested those compounds could be regarded as models of intermediate stages of S_N2 substitution at silicon. Corriu⁸⁹ and Frye² did find that the hydrolysis of a range of chlorosilanes was first order in nucleophilic catalysts such as Py, HMPA and DMF etc.. They criticised the mechanism proposed by Allen and Modena for hydrolysis and methanolysis of silyl



Scheme 1.11 Allen and Modena mechanism.

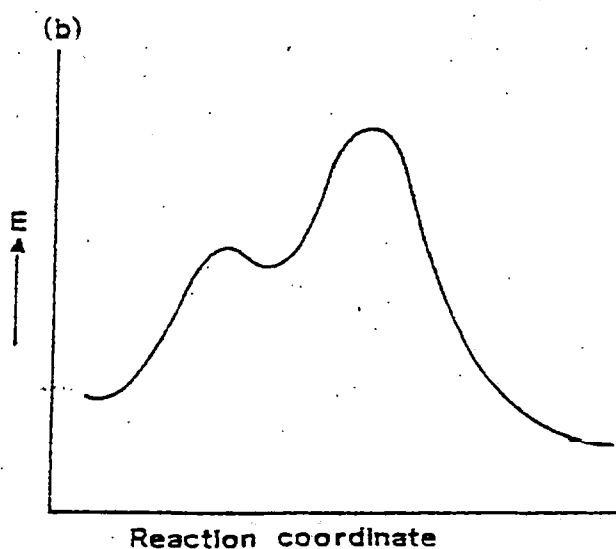
chlorides involving base catalysis^{90a}, as shown in **22**, that it could not explain the common mechanism for nucleophile-catalyzed hydrolysis and racemization and that the rate of hydrolysis depends not on the basicity but the nucleophilicity of the nucleophile. Nevertheless, Holmes^{77, 90b} believes that hydrogen-bonding plays an important role in the pentacoordinate transition state in a sol-gel process. Chojnowski^{90c} reports that an uncharged nucleophile can function as a general base. Recently Tamao *et al*^{90d} even presented an interesting equilibrium between tetra- and pentacoordination by a bridged fluorine, see Scheme 1.12. The geometries of both silicon atoms of **23** are in the middle of the reaction coordinate for the tetrahedral to the TBP transformation.



a i. S_N2 -C Transition state

ii S_N2 -Si Transition state

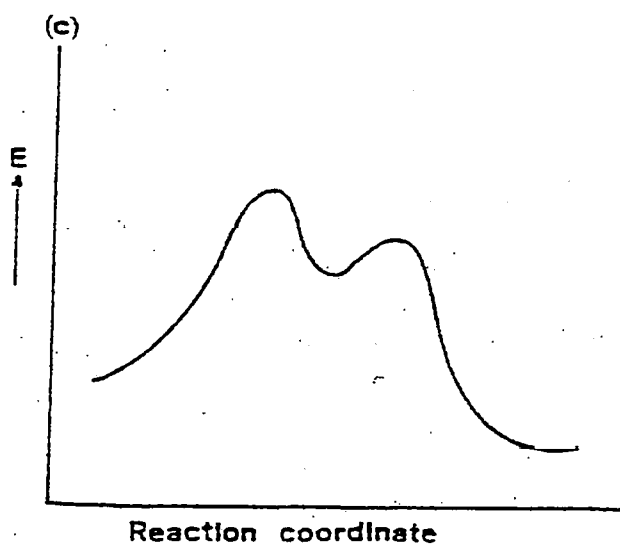
$$\text{Rate} = k_2 [\text{R}_3\text{SiX}] [\text{Nu}]$$



b S_N2^* -Si

Rapid pre-equilibrium formation of a five coordinate transition state, followed by rate limiting conversion to products.

$$\text{Rate} = k_1 k_2 [\text{R}_3\text{SiX}] [\text{Nu}]$$

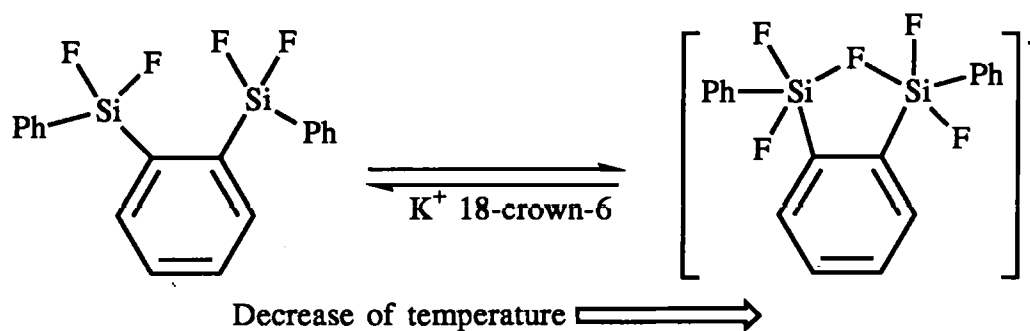


c S_N2^{**} -Si

Rate determining formation of pentacoordinate intermediate, followed by rapid dissociation to products.

$$\text{Rate} = k_1 [\text{R}_3\text{SiX}] [\text{Nu}]$$

Figure 1.8 Profiles of the S_N2 process at silicon



Scheme 1.12 Tamao scheme.

Corriu^{82, 83} suggested, on the basis of kinetic studies, that the formation of a pentacoordinate intermediate was rate determining (S_N2^{**} -Si, Figure 1.8c) and that the S_N2 -Si process (Figure 1.8a) was rare for silicon.

Sommer^{3b} has also suggested an S_Ni -Si mechanism (see 14) to describe the retention of configuration involving a quasicyclic pentacoordinate transition state / or intermediate. However Corriu^{82, 83} argued against such a process. The fact that the addition of Li^+ complexing agents to coupling reactions between silanes and organolithium compounds results in an increase of the proportion of inversion is in contradiction with the effect in Li^+ in an S_Ni -Si process. Nevertheless it still holds most of its ground.

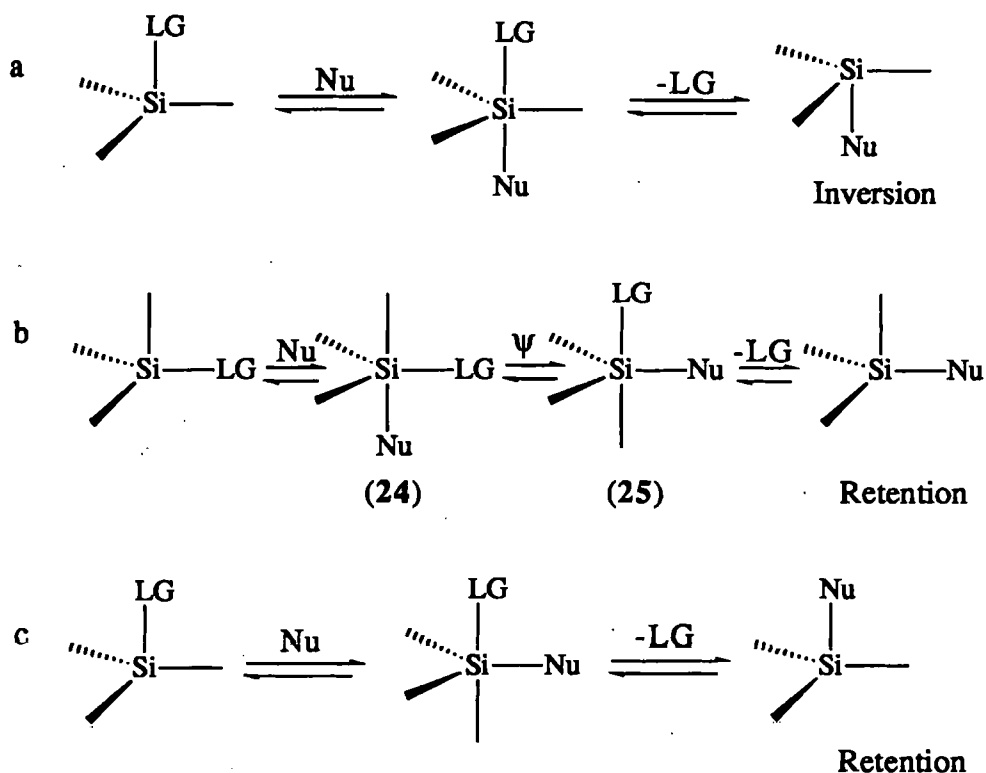
(II) Involving pseudorotation

The pseudorotation, mainly the Berry pseudorotation (see Scheme 1.5), process has been well established as a mechanistic process in phosphorus chemistry⁹¹. In order to interpret the stereochemistry of organic silicon, Prince⁹², Sommer⁹³, Fleming⁹⁴, Corriu⁷⁶, Armitage³⁸, Bassindale⁷⁸ and Holmes⁷⁷ et al have adopted such a process for the pentacoordinate transition state / or intermediate. The rules laid down for governing substitution at phosphorus may be applied to silicon^{77, 78, 91a}:

- (i) Entry of nucleophiles and departure of leaving groups occurs in the apical positions.

- (ii) Electronegative substituents prefer apical positions.
- (iii) Four and five-membered rings are constrained to span one apical and one equatorial positions.

Inversion of configuration can be obtained without pseudorotation when the attacking nucleophile and the leaving group are both apical as shown in Scheme 1.13a.



Scheme 1.13 Mechanisms for nucleophilic substitution at silicon.

* ψ indicating a pseudorotation.

Considering that the bonds at the apical position in a TBP are more ionic, longer and easier to stretch, there is no wonder why inversion is more often observed. Retention of configuration needs a pseudorotation after the Nu axially attacking next to the LG from 24 to 25 (see Scheme 1.13b). Applying rule (ii), it seems the pseudorotation process in this case might be energetically unfavourable as electronegative substituents are forced into equatorial positions. Consequentially, Corriu^{82, 83, 95} advanced an edge attack with the incoming nucleophile situated directly equatorial

(see Scheme 1.13c). However, the Berry pseudorotation does not have a high energy barrier either theoretically or experimentally. Martin⁹⁶ has shown that pseudorotation has a lower barrier than that of the corresponding phosphorus. Bassindale⁷⁸ summarized the energy barriers to ligand exchange within a range of pentacoordinate silicon compounds and proposed that the lower-energy pathway came from pseudorotation whereas the higher-energy process arose from dissociation. The barrier to pseudorotation seems to depend on the number of electronegative groups present and their electronegativity:

Monofunctional
 $\Delta G^\ddagger > 20$

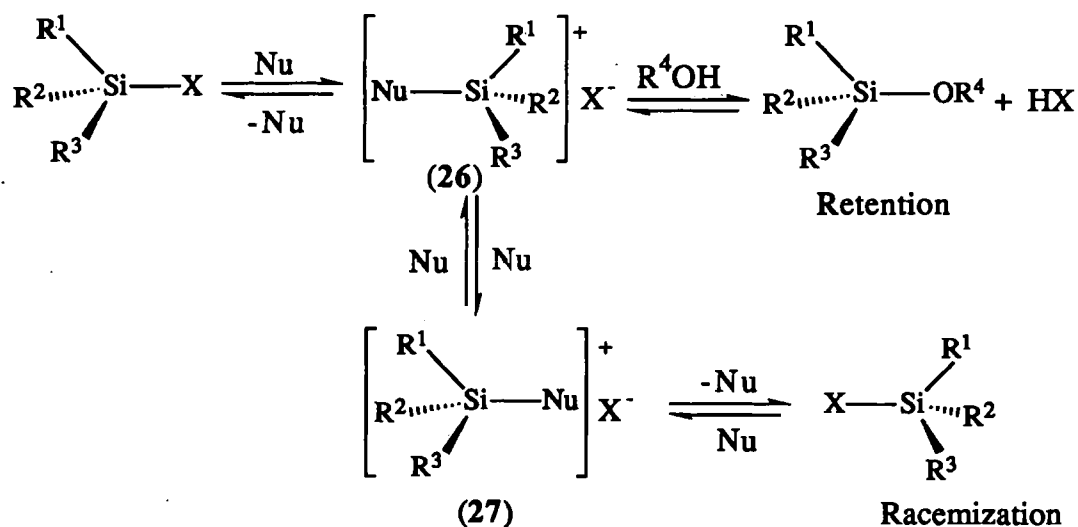
Bifunctional
 $\Delta G^\ddagger \sim 9-12$

Trifunctional
 $\Delta G^\ddagger < 7$

Holmes^{77,84} has strongly argued against edge attack. He pointed out that axial attack followed by a pseudorotation was a more energetically favourable pathway. The apicophilicities of the leaving group of silicon, different from those of phosphorus, changed with the attacking nucleophiles. Soft nucleophiles, for instance, increased the apicophilicity of the leaving group and hence promoted inversion. Corriu^{82b} has also found that the stability of compounds **17** increased with apicophilicity of the group at the site *trans* to the donor nitrogen atom. The rate enhancement and preference to retention of strained, saturated four and five-membered rings at silicon verify rule (iii) as well, though in cases of extremely steric encumbrances and strong nucleophiles equatorial departure might be forced to perform⁹⁷. Therefore the rules of pseudorotation for phosphorus are very useful and, indeed, suit silicon rather well.

(III) Involving ionic tetracoordinate species

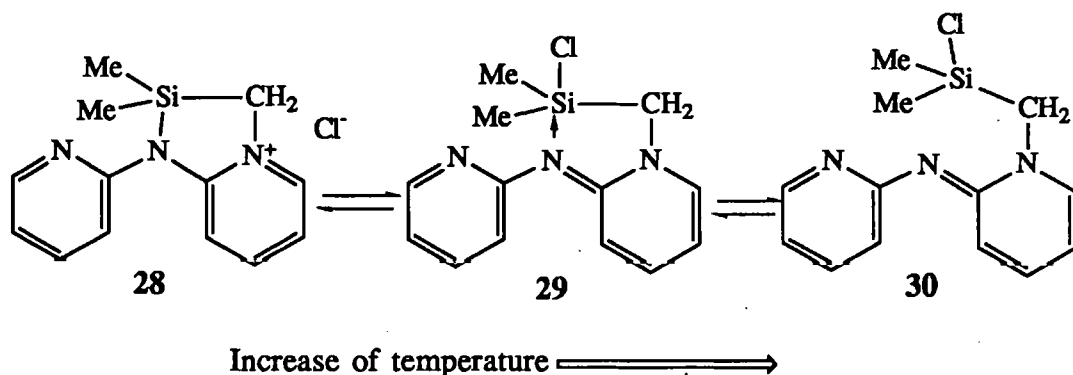
Chojnowski⁵ proposed that an ionic tetracoordinate species was the key pathway for nucleophile-catalysed racemisation and substitution. His isolation of the salts $[\text{Me}_3\text{SiHMPA}]^+ \text{X}^-$ ($\text{X} = \text{Br}, \text{I}$), conductivity studies and examination of the racemization of (1-Naph)PhMeSiCl⁹⁸ led him to conclude that **26** or **27**, see Scheme 1.14, were the crucial intermediate. Frye's kinetic study of the alcoholysis of



Scheme 1.14 Chojnowski mechanism

$\text{Ph}_2\text{SiCl}_n(\text{OR})_{2-n}$ ($n=1, 2$) strongly supported such an idea². Hensen⁵² supplied crystal structure of some typical ionic tetracoordinate adducts. Bassindale and Stout^{51, 99} clearly demonstrated the existence of $[\text{Me}_3\text{SiNu}]^+ \text{X}^-$ in solution and the relationship between the ability to form adducts and the ability to catalyse nucleophilic substitution of the nucleophiles. Further studies^{6,100} have shown that the cationic tetracoordinate species was highly susceptible to nucleophilic attack, though stereochemically rigid. As a result, an extension to the double displacement mechanism was proposed, see page 3 Scheme 1.2. What Corriu¹⁰¹ criticized on the conductivity behaviour can be related to the effects of the solvation of the tight ion pairs⁹⁹.

Although the ionic tetracoordinate intermediate is the key to this mechanism, it is conceivable that an expansion of coordination must be existing at some stages. Indeed, Bassindale¹⁰² reported the observation by NMR spectroscopy of simple acyclic pentacoordinate silicon salts $[\text{Me}_2\text{HSiNu}_2]^+ \text{OTf}^-$ ($\text{Nu} = \text{NMI}, \text{Py}, \text{DMAP}$). A better example comes from Kummer's study of $\text{RN}-2-(\text{C}_5\text{H}_4\text{NCH}_2)_2\text{SiMe}_n\text{X}_{3-n}$ ($\text{R} = 2-\text{C}_5\text{H}_4\text{N}$, $\text{X} = \text{Cl}, \text{Br}$, $n = 1, 2$). In solution, see Scheme 1.15, the formation of the ionic tetracoordinate salt (28) and the neutral pentacoordinate adduct (29) was



Scheme 1.15 Kummer scheme.

highly temperature dependent. Therefore it is reasonable to suggest, as Corriu did¹⁰¹, that the ionic four-coordinate intermediate may only operate with good leaving groups and nucleophiles.

(IV) Involving further expansion of coordination

Corriu^{4, 89b, 101} has correlated the kinetic laws, the high negative activation entropy and stereochemistry of the racemization and nucleophilic substitution with further expansion of coordination to form a hexacoordinate transition state / or intermediate, see Scheme 1.1. This mechanism implies that:

- (i) the pentacoordinated species **1** must be pre-equilibrium and stable;
- (ii) **1** must react faster with the second nucleophile (alcohol in the case of alcoholysis or the nucleophilic catalyst in case of racemization) than the starting tetracoordinate silane as a result from catalytic acceleration;
- (iii) the rate-determining step is the nucleophilic attack on **1** forming a hexacoordinate intermediate / or transition state, of which the bond between the incoming nucleophile and silicon is formed during the breaking of the bond between the silicon and the leaving group.

Evidence in favour of this mechanism comes from a variety of sources. As **2** and **3** both have a plane of symmetry, the reversible formation of such species leads to inversion or retention of configuration with equal probability. The racemization is second order

with respect to the nucleophile whereas alcoholysis is first order in alcohol and nucleophile respectively. The large negative values of the entropy of activation demand a highly organized intermediate / or transition state, which matches the character of six-coordination. All these agree with this mechanism. Holmes *et al*¹⁰⁶ have also adopted such a mechanism in some reactions. As this model is so powerful, Corriu^{65, 101b} even suggested that nucleophilic attack on a hexacoordinate silicon atom via heptacoordination cannot be eliminated.

However, although it is possible for silicon to expand its coordination, not all silicon compounds are able to extend to six-coordination. For example, Martin^{96, 105} found

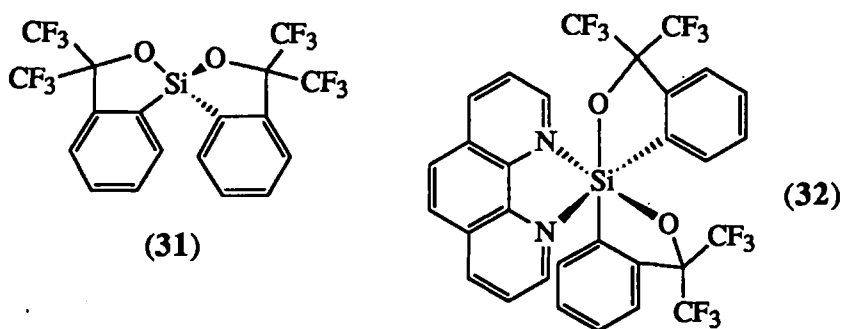


Figure 1.9 Typical compounds.

little evidence of hexacoordinate adducts in the reactions of compound 31 and various nucleophiles, with one exception (see 32) though¹⁰³. He pointed out that the racemization of 31 was via pentacoordinate pseudorotation. Therefore the application of such mechanisms involving hexa- or heptacoordinate intermediates is inevitably limited. Frye², Cartledge¹⁰⁴ etc. have also argued against this idea to certain degree.

1.4 Reactivity of hypercoordinate silicon and Si-H bond

In the mechanisms of nucleophilic substitution at silicon discussed above, the expansion of coordination of silicon is always involved. This fact certainly leads to the

question of the reactivity of hypercoordinate silicon compounds. Indeed, the enhanced reactivity of penta- and hexa-coordinate silicon species has gained more and more attention in recent years^{77, 105}. Meanwhile, SiH, as a special bond involved in reductive reactions, has also been found to be of renewed interest.

1.4.1 Enhanced reactivity of hypercoordinate silicon compounds

The silicon centre at a penta- or a hexa-coordinate state is intuitively sterically hindered to a greater extent and less electrophilic than at a tetracoordinated one.

However, both calculations^{106, 107} and X-ray analysis³⁵ have shown that the bond lengths become considerable longer when the coordination number surrounding silicon increases from four to five. The elongation of bonds, particularly the apical ones, in addition to the large size of silicon (compared with carbon) reduces the steric hindrance of the hypercoordinated silicon undergoing nucleophilic attack. Damrauer *et al*¹⁰⁸ studied $[RR'SiF_3]^-$ with ^{19}F NMR and revealed that steric effects on the exchange barriers were generally very small indeed.

The most striking feature of pentacoordinate silicon compounds by calculation is that the positive charge on silicon atom remains unchanged or slightly increased³⁵. Calculations at various levels on the $SiH_4-[SiH_5-nF_n]^-$ systems^{40, 84, 106, 107, 109} showed that the positive charge has just a very small or even effectively no change at the central silicon atom when it increases from tetra- to penta-coordination. However the addition of fluoride ion causes an increase in negative charge on all substituents. Gronert *et al.*⁴⁰ preferred an ionic model and stated that “the silicon acts more as a central cation rearranging its ligands to create a further coordination site than as a covalently bound atom expanding its valency”. A similar result can be drawn by applying the four-electron three centre model to the pentacoordinate silicon species. It is reported that X-ray fluorescence spectra revealed a higher positive charge on the silicon atom of silatranes $XSi(OCH_2CH_2)_3N$ compared to $XSi(OCH_2CH_3)_3$ ¹¹⁰.

On the whole, the general loosening of all bonds, maintenance of electrophilicity of the

silicon centre and reinforcement of the leaving ability of the LG together result in an enhanced reactivity of hypercoordinate silicon compounds. This enhanced reactivity is not only relevant to substitution mechanisms of silanes but is also manifested in reactions of specific hypercoordinated silicon complexes.

Corriu and co-workers have supplied a good part of the evidence¹¹⁵. They found that 18-crown-6 potassium salts of $\text{Ph}_3\text{SiF}_2^-$, MePhSiF_3^- and pentacoordinated alkoxysilicates reacted more readily with strong nucleophiles (RLi , RMgX , H^- , RO^-) compared to the corresponding tetracoordinate derivatives¹¹¹. MePhSiF_3^- , for instance, underwent alkylation with *i*-PrMgBr to give $\text{MePh}(i\text{-Pr})\text{SiF}$ more than 150 times faster than the analogous reaction with MePhSiF_2 . They reported that complexes $\text{Na}^+[\text{RSi}(o\text{-OC}_6\text{H}_4\text{O})_2]^-$ ($\text{R} = \text{Me}$, Ph , 1-Naphthyl) were very reactive towards nucleophilic reagents such as organometallic reagents and hydrides¹¹². They demonstrated that tris(benzene-1,2-dioxolato)silicon reacted very rapidly with Grignard or organolithium or reducing agents (LiAlH_4 , for an example) and created an alternative route for preparation of organosilanes from SiO_2 or Na_2SiF_6 ¹¹³. They attributed the nucleophilic activation of silyl enol ethers and esters to the formation of a crucial pentacoordinated intermediate¹¹³. They suggested the Si-N bond formation by dehydro-coupling of Si-H and N-H in the presence of a nucleophile was activated by pentacoordination^{114a}. Holmes and co-workers^{77, 90b} have also showed that an acetone solution of $[\text{Mes}_2\text{SiF}_3] [\text{K}\cdot 18\text{-crown-6}]$ ($\text{Mes} = \text{Mesityl}$) reacted with water at room temperature in a matter of minutes, whereas Mes_2SiF_2 was essentially unchanged after 24 hours under similar conditions. Voronkov^{114b} suggested that the ease of ring closure of $[\text{Me}_2\text{HSi}(\text{CH}_2)_3\text{NHR}]$ to form 1-aza-2 silacyclopentanes was the result of intramolecular Si...N interaction. Kira *et al*¹¹⁵ believed that the regiospecific and highly stereoselective allylation of aldehydes and α -hydroxy ketones with allyltrifluorosilanes or allyltrialkoxysilanes was activated by the cyclic hypercoordinate intermediates **33** and **34** (see Figure 1.10). Corriu¹⁰⁵ pointed out that the reactivity of pentacoordinate silicon complexes paralleled their ability to expand their coordination number to six. Pentacoordinated silatranes and **31**, for instance, are

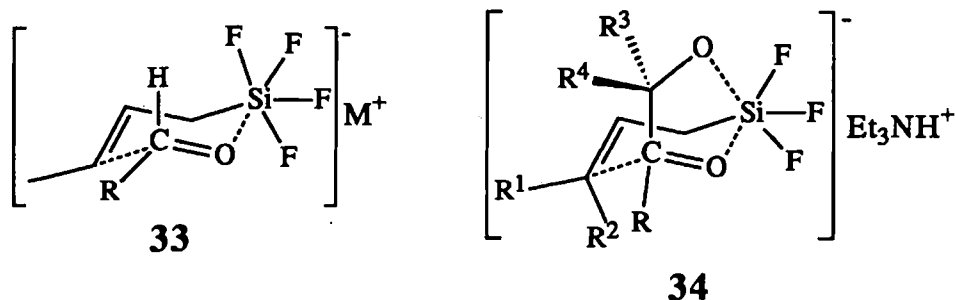


Figure 1.10 Kira allylation intermediates.

reluctant to extend their coordination, hence they are relatively chemical inert¹¹⁶. He suggested the differences of activity did not come from the anionicity but the structure of the pentacoordinated complexes. Overall, enhanced reactivities of hypercoordinate silicon species are common.

1.4.2 Reactivity of Si-H Bond

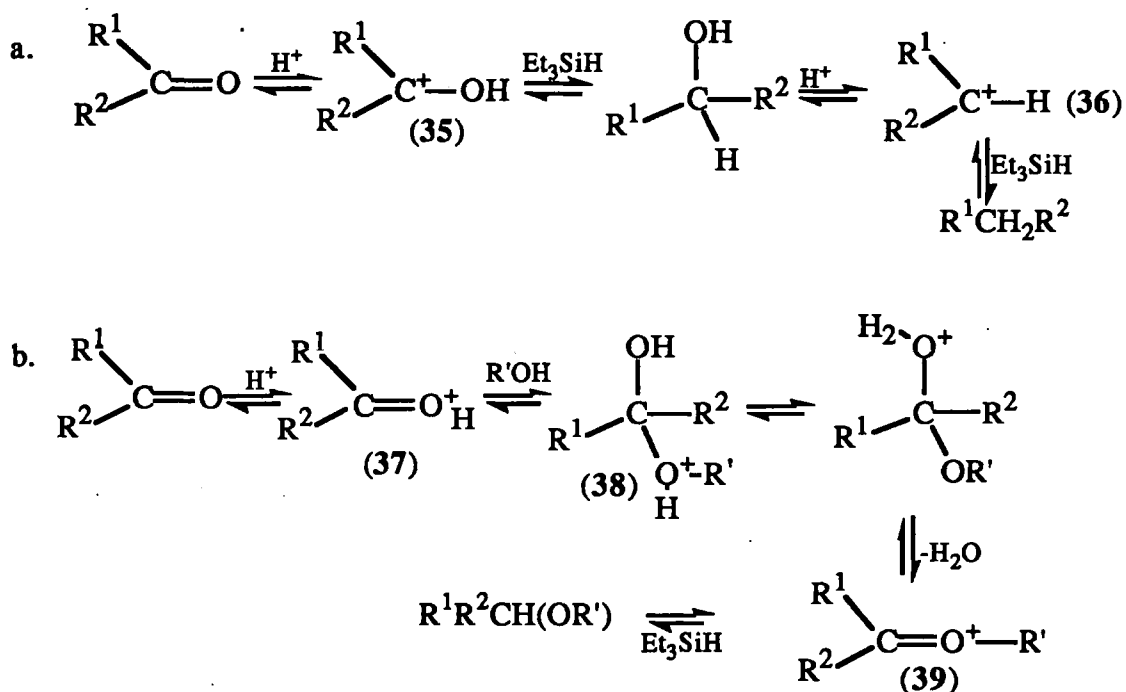
The addition of the silicon-hydrogen bond to unsaturated functional groups, classified as reduction, is a useful and developing routine in organic synthesis^{8, 13}. The reaction, which usually needs catalysts to control the reactivity and selectivity, can be induced in a variety of ways, including heating, light, peroxides, transition metal complexes, metals, acids amines and other nucleophiles or salts. Electronegative groups on silicon help the reaction with a general reactivity sequence of Cl₃SiH > Cl₂MeSiH > Et₂SiH₂ > Et₃SiH²⁴. The following is just an abstract of the reduction reaction involving coordination of silicon in the sense of donor-acceptor interactions in solution.

(I) Ionic activation of Si-H bond

It is suggested that Si-H bond addition can be activated without expansion of coordination of silicon and can be used as a reducing agent under both acidic and basic conditions⁸.

Kursanov¹¹⁷ and West¹¹⁸ reported that, in the presence of trifluoroacetic acid, triethylsilane reacted with cyclohexanone to yield cyclohexanol via trifluoroacetoxy-

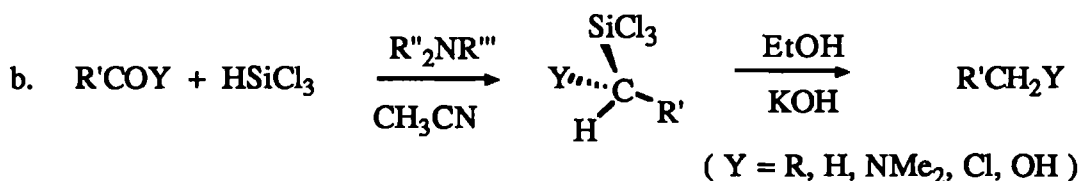
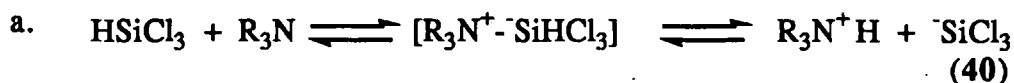
cyclohexane and with acetophenone or benzophenone to yield phenylethane or diphenylmethane. The reaction was supposed to proceed by initial protonation of the carbonyl group to produce a stabilized carbocation (35) which reacted with the silane, as shown in Scheme 1.16a. The silane essentially acts as a H^- supplier in these cases.



Scheme 1.16 Acidic reduction of carbonyl groups with Si-H.

Ketals and acetals reacts with R_3SiH under similar conditions (in the presence of acids or Me_3SiOTf) in the same way but yields an ether¹¹⁹. The competitive formation of ether from the reduction of aldehydes in acidic addition is overwhelming¹²⁰. Nevertheless, the pathway proposed by Doyle^{119a}, see Scheme 1.16b, does not alter the position of the H-containing silanes.

In contrast to the incorporation of acids with lower electronegatively substituted silanes, namely R_3SiH , in the reduction reactions, bases, mainly tertiary amine, were co-used with more electronegatively substituted silanes, say HSiCl_3 . Benkeser¹²¹ has elucidated much of the chemistry of such a system. He proposed that the key intermediate of trichlorosilane and tertiary amine in solution, in the reduction of



Scheme 1.17 Benkeser reduction schemes.

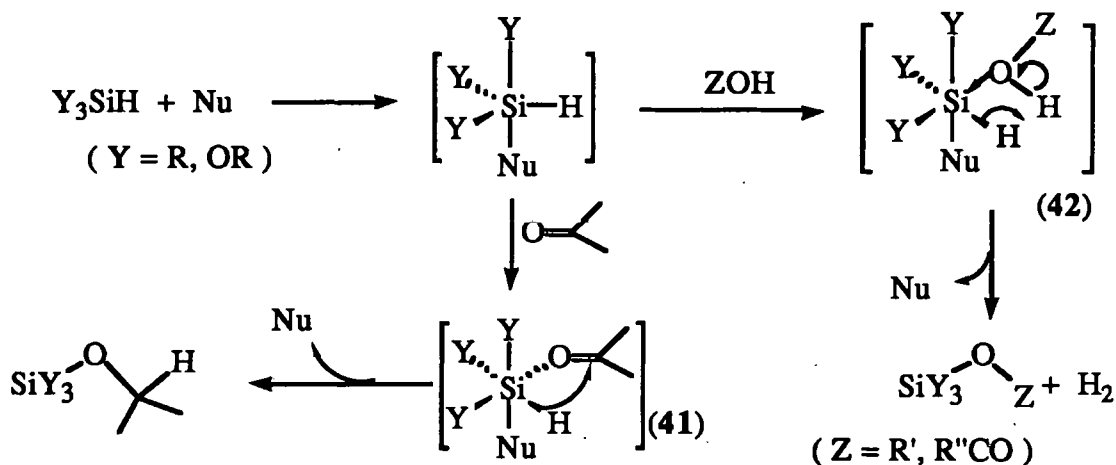
polyhalogenated alkanes¹²², carbonyl compounds¹²³ (see Scheme 1.17b) and addition of olefins and acetylenes¹²⁴, was the trichlorosilyl anion $^-\text{SiCl}_3$ which acts as a nucleophile (see Scheme 1.17a). ^1H NMR has shown the existence of such anions and supported this suggestion¹²⁵. Recent infrared matrix isolation studies¹²⁶ have indicated that bases were bonded to Si-H bond, though largely coordinated to the silicon centre. As HSiCl_3 is known to be facile in forming coordinated complexes and mechanistic studies have not been carried out, this mechanism is still open to question. For example, Corriu *et al*¹²⁷ prefers a hypervalency interpretation even with much less electronegatively substituted silanes, such as 1-NaphMeSiH and di-, tri-hydrogenosilanes, when they reacts with hydrides.

(II) Hypercoordinate activation of Si-H bond

The enhancement of reactivity of hypercoordinated silicon compounds is equally applied to the activation of Si-H bonds.

Hata and co-workers¹²⁸ found pentacoordinated bis(diolato)hydridosilicates, derived from trichlorosilane and catechol or 2,2'-dihydroxybiphenyl in THF, could reduce aldehydes and ketones without any catalyst in high yield. Similar results were reported with trialkoxysilane and alkoxides of alkali metals¹²⁹. Corriu and co-workers^{130, 131} have actually prepared the anionic hydridosilicates $[\text{HSi}(\text{OR})_4]^- \text{K}^+$ and dihydridosilicates $[\text{H}_2\text{Si}(\text{OR})_3]^- \text{K}^+$ by coordination of KOR or KH to $\text{HSi}(\text{OR})_3$ without addition of 18-crown-6. They demonstrated that both $\text{HSi}(\text{OR})_4^-$ and $\text{H}_2\text{Si}(\text{OR})_3^-$, in

addition to their behaviour as single electron transfer agents and sensitivity to water with loss of H_2 , reacted as electrophilic centres readily with aldehydes and ketones to yield alcohols, and with Grignard and organolithium reagents to yield substituted silanes. They proposed a mechanism for reduction of carbonyl and alkoxyl groups with Si-H bond and nucleophilic catalysts involving penta- and hexa-coordinate intermediates, see Scheme 1.18. Kinetic studies have supported this mechanism



Scheme 1.18 Corriu reduction mechanism.

as well¹³². Corriu¹⁰⁵ suggested that the oxidants themselves also had a general reactivity order of aldehydes > ketones > esters > alcohols. It is noticeable that the reducing power of the pentacoordinated Si-H containing complexes does not arise from their anionicity. Corriu's work¹³³ on neutral pentacoordinate compounds, such as derivatives of 17, 43, 44 (X = R, Y, Z = H) clearly showed they are able to act as

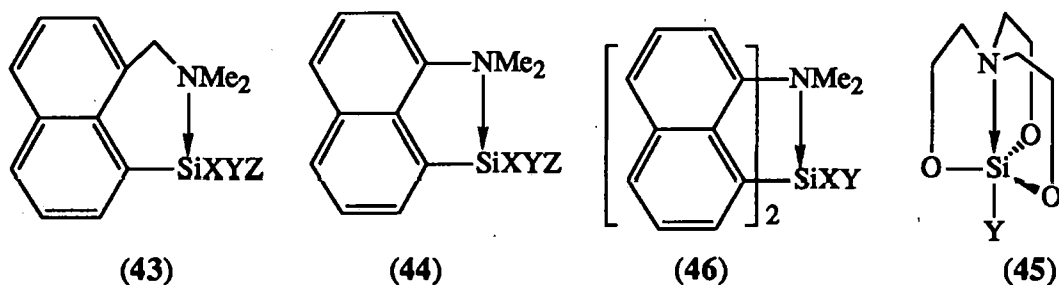


Figure 1.11 Typical neutral hypercoordinated silicon compounds.

reducing agents by a simple exchange of Si-H bond in the pentacoordinate complexes (via hexacoordination) with acyl chlorides, acids, carbon dioxide to yield aldehydes, with aldehydes, ketones to alcohols, and with alcohols to alkoxysilanes.

However, it is noted that not all hypercoordinated silicon species are so reactive.

Neutral pentacoordinate **45** (Y = H) takes days under reflux to reduce carbonyl groups to alcohols¹³⁴. Pentacoordinated anionic hydride of **31** does not react with carbonyl groups in the absence of electrophilic activation of >C=O group¹³⁵.

Hexacoordinate **46** (X, Y = H) is completely chemically inert toward strong nucleophiles and carbonyl groups¹¹⁶. Although it is suggested that these differences of reactivity might be related to their particular individual structures¹⁰⁵, satisfactory explanations are not available yet.

1.5 ²⁹Si NMR in the study of reaction mechanisms

Nuclear magnetic resonance (NMR) spectroscopy is a powerful method for molecular structure determination. Silicon-29 is especially important in studying mechanisms and complexation of nucleophilic reactions of silicon and there is no rival for the detection of silicon atoms in different molecular environments. Used together ¹H and ¹³C, ²⁹Si NMR and DNMR can not only determine the rather complex structures of organosilicon compounds, but also elucidate the reaction mechanisms with confidence. There are several reviews on this subject¹³⁶ and most recently by Williams¹⁰ and Tandura *et al*³⁵. The following is just a brief summary of the application of NMR in the study of the mechanisms of the nucleophilic reactions and coordination of silicon.

1.5.1 The silicon-29 NMR technique

The early NMR work was concentrated on elucidating structures using proton NMR. It was not until the availability of Fourier transform (FT) and the development of improved multinuclear NMR in the 1970s that led to a dramatic increase in the

observation of less abundant and lower sensitive nuclei such as silicon-29 and carbon-13. Nonetheless, difficulties are still encountered in measuring and understanding silicon-29 NMR.

Silicon-29 ($I = 1/2$) has a low natural abundance of 4.67% and a negative gyromagnetic ratio γ of -0.555, which means that under proton decoupling conditions the nuclear Overhauser effect enhancement (NOE) is negative, resulting in a reduction or cancellation of the signal intensities or even negative signals of ^{29}Si . Its characteristic long spin-lattice relaxation (T_1) prolongs the data accumulation times, which hinders the observation of ^{29}Si NMR signals.

Fortunately, there are methods to overcome these problems.

Transition metal complexes such as chromium or iron acetylacetonates (acac) are often used in low concentration (ca. 1%) as paramagnetic relaxation agents, which serves to replace other relaxation mechanisms with the highly efficient electron-nuclear dipole-dipole interaction, reducing T_1 and remove successfully the NOE. However, there is a drawback of this approach, in that these reagents may contaminate the sample under investigation, and undesirable side reactions are possible especially with those reactive organosilicon species.

With the development of computer technology, the design of special pulse sequences¹¹ has provided ways of greatly increased sensitivity. In particular the polarization transfer techniques^{137a} have been proved to be very useful, which transfer the induced nuclear spin polarization upon a weak irradiation of a sensitive nucleus with a large gyromagnetic ratio γ , high abundance, rapid relaxation and considerable Boltzmann population difference, *eg.* proton, to a insensitive one such as silicon-29. Helmer and West¹³⁷ employed INEPT (insensitive nuclei enhanced by polarization transfer) pulse sequences to a range of silanes and found enhancement factors of up to 9. Nevertheless, these techniques need one or more protons coupling to silicon-29. What's more, the enhancement is governed by the pulse parameters, which can be

evaluated from the ^1H - ^{29}Si coupling constants. Improper use of these parameters may lead to signal distortion or cancellation.

The high fields available from superconducting magnets can improve the sensitivity of silicon-29 NMR. Substantial advances in high resolution NMR of solids have also led ^{29}Si NMR to be invaluable for studying hypercoordinate silicon in solid state^{136d}.

1.5.2 NMR properties of coordinate silicon compounds

Tetramethylsilane (TMS) is the most commonly used reference compounds for ^{29}Si as well as for ^1H and ^{13}C . The presently known silicon chemical shift range, including the extreme cases, is 825 ppm relative to TMS at $\delta^{29}\text{Si} = 0$ ppm with positive values to high frequency (low field) and negative values to low frequency (high field). Most silicon chemical shifts actually occur in a much smaller range from +50 to -190 ppm¹⁰.

The greatest effect on ^{29}Si chemical shifts results from changes in coordination number at the silicon atom^{10, 35}. Generally, four-coordinate silicon with organic substituents is in the +45 to -115 ppm region of the spectrum. All experimental data for coordination number of silicon more than four display ^{29}Si signals at a much higher field compared with their tetracoordinate analogs. The silicon chemical shifts of the five-coordinate silicon compounds are generally in the -50 to -150 ppm region while the six-coordinate species usually appear at a even lower frequency from -130 to -200 ppm (see Figure 1.12). Therefore, silicon-29 NMR has provided an excellent method to study the equilibria between normal four-coordinate silanes and hypercoordinate species in solution as well as characterizing these compounds as penta- or hexa-coordinate silicon compounds^{10, 35}.

The effect on ^{29}Si chemical shifts caused by substitution changes directly at silicon is secondary relative to the alteration of coordination number and should be interpreted with care. It is pointed out¹³⁹ that electronegative substitution of methylsilanes causes a deshielding of the silicon nucleus but the correlation between the silicon chemical

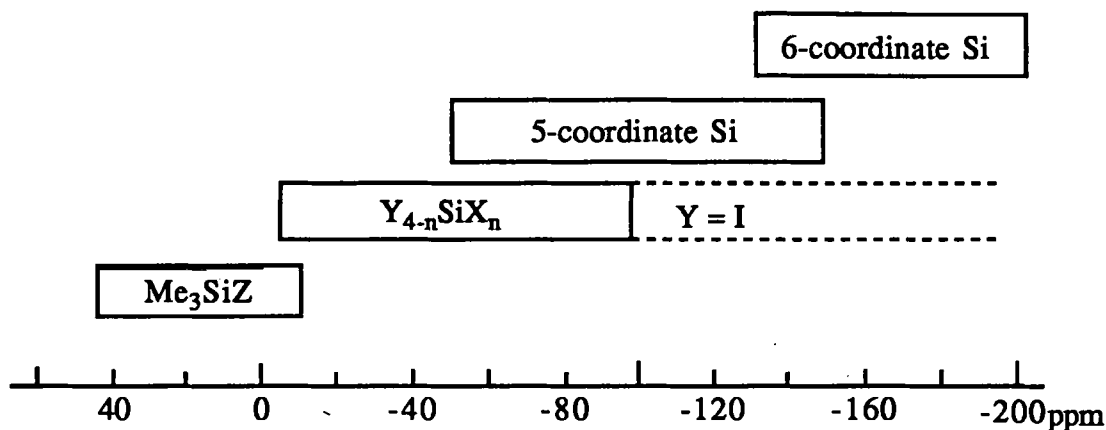


Figure 1.12 Silicon-29 chemical shift ranges for various organosilicon.

Z = Organic group; X, Y, = F, Cl, Br.

shifts ($\delta^{29}\text{Si}$) and substituent electronegativity (χ_x) is poor. As a matter of fact, a plot of the total substituent electronegativity for all silanes versus their chemical shifts shows U-shaped curves¹³⁶. The successive substitution of methyl groups by chloride, for example, displays an initial increase, followed by gradual decrease of silicon chemical shifts (Me_4Si , 0.0 ppm; Me_3SiCl , +30 ppm; Me_2SiCl_2 , +32 ppm; MeSiCl_3 , +12.5 ppm; SiCl_4 , -20 ppm).

The geometry of the silicon compounds can also affect ^{29}Si chemical shifts. It is known³⁵ that donor-acceptor interactions forming neutral complexes usually cause smaller changes in $\delta^{29}\text{Si}$ (less than 70 ppm) than in the cases of ionic species. However, structurally similar neutral and cationic as well as cationic and anionic species with hexacoordinated silicon atoms bonded only to oxygen atoms have nearly identical ^{29}Si chemical shifts¹⁴⁰. This is attributed to the symmetric arrangement of the ligands in a coordinate octahedron, which effectively quenches any charges on the central atom. It is found¹⁰ that the chelate ring size of cyclic silicon species is important with a trend for a deshielding effect when the ring strain increases. It is also reported that there is a dependence of the chemical shifts on the arrangement of silicon bonds among non-equivalent positions (equatorial and axial) in a TBP, though not in a great magnitude³⁵.

There exists a small difference in ^{29}Si chemical shifts between different solvents (less than 5 ppm). Williams and co-workers¹⁴² found a good linear correlation of the chemical shifts of a series of silanols and silylamines against the Gutmann donor number⁸⁶. Such changes in chemical shifts are normally thought to arise from an increase in electron density at silicon by interactions of the type $\text{R}_3\text{Si}-\text{O}-\text{H} \leftarrow \text{Donor}$ together with repulsion of the O-H bonding electrons with the donor solvent electron pair.

There is yet no comprehensive theory advanced to explain all $\delta^{29}\text{Si}$ data. Schraml and Bellama^{136b} suggested that the chemical shifts of silicon-29 were dependent upon the electric field, magnetic anisotropy of the neighbouring groups and the polarization of the Si-X bonds, governed by the electronegativities of the substituents. For example, the inductive effect of substituents caused a decrease in nuclear shielding whilst a (p-d) π interaction resulted in back donation and thus increased shielding around silicon.

According to the variations of the paramagnetic terms proposed by Engelhardt *et al*¹⁴¹, ^{29}Si shielding is parabolically related to the total electron charge on tetrahedral silicon atom. When the silicon atom is surrounded by electronegative substituents, the ^{29}Si resonance is displaced upfield with a decrease in negative charge. This is applicable to pentacoordinate silicon species because it is possible that silicon at a five-coordinated centre has an enhanced positive charge and the electron density at the acceptor atom (Si) may be transferred to other parts of the acceptor components. Tandura *et al*³⁵ pointed out that it was the substituents rather than any simple donor-acceptor inductive effects that dominate the ^{29}Si chemical shifts upon extracoordination. However, no exact relationship has been found between the increasing chemical shifts and the increasing of the coordinate interactions of the silicon atom.

Although the high sensitivity of silicon-29 resonance to a change in coordination number of silicon is a simple and reliable way of establishing intra- and intermolecular coordinate interactions in molecules, the data of ^{13}C , ^1H , ^{19}F and ^{31}P chemical shifts as well as $^{29}\text{Si}-^1\text{H}$, $^{29}\text{Si}-^{19}\text{F}$ and $^{29}\text{Si}-^{31}\text{P}$ coupling constants are a valuable help to

decide structures that are otherwise ambiguous.

The resonances of carbon atoms of organic silicon compounds differ from normal organic species in some degree. The ^{13}C chemical shifts of SiCH_3 , for example, occur between -15 to +20 ppm with an unusual shielding and each subsequent replacement of a methyl group of SiMe_4 with a chlorine atom produces a “sagging pattern” curve, like those of silicon-29^{139a}. The formation of extracoordinate complexes can alter the ^{13}C resonance frequency, especially the ones adjacent to silicon. It is found from the much studied silatranes that $\delta^{13}\text{C}$ values of the carbon atom attached to pentacoordinate silicon are always greater than in the case of tetravalent silicon analogs³⁵. The ^{13}C chemical shifts of the donor moiety usually move to lower field upon coordination. The coordinate interaction of the type $\text{Si} \leftarrow \text{O}=\text{C}$, for instance, results in a lower field of ^{13}C resonance of the carbonyl carbon. Nonetheless, the ^{13}C data are complicated and need to be dealt carefully while coordination information is provided.

It is well known that proton chemical shifts are largely determined by electronic effects¹⁴³. Therefore, the resonances of protons of organosilicon compounds often show a strong shielding and substantially depend on the electronegativities of the substituents and solvents¹⁰. Phenylsilanes have two sets of multiplets between 7.1 and 7.8 ppm with the more shielded *ortho* and *para* at the higher field, by contrast to the singlet of most alkyl monosubstituted benzenes. The coordinate interaction, $\text{Si} \leftarrow \text{:D}$, strengthening the ionic character of the covalent silicon bonds, enhances the electron density on the atoms or groups attached to the silicon and results in a general increase of proton shielding. The magnitude of the multiplet separation of phenyl-substituted species increases accordingly when the silicon passing from tetracoordination to hypercoordination.

In addition to the characteristic proton resonance, it is possible with Si-H containing species to observe the ^{29}Si satellites. These coupling constants usually range from 147 to 381 Hz and show a general trend of increasing J_{SiH} with increasing electronegativities of substituents on Si^{136d}. It is proposed³⁵, silicon on going from

tetracoordination to pentacoordination, that an equatorial arrangement of Si-H bond with an enhanced s-character was responsible for an increase of J_{SiH} and an axial position corresponded to a decrease of J_{SiH} values.

The ^{19}F NMR spectra of penta- and hexa-coordinate silicon compounds containing Si-F bonds normally exhibit a singlet due to fast intra- and inter-molecular exchange¹⁴⁴. The chemical shifts move towards downfield when the coordination number of silicon increases (SiF_4 , -160ppm; SiF_5^- , -136 ppm, SiF_6^- , -128 ppm). The coupling constants also decrease as the s- and p-character of the bonds reduced in a hypercoordinated silicon complex. At lower temperature, ^{19}F signals in pentacoordinate species shift downfield when F is at an apical position and upfield in the case of equatorial¹⁴⁵. In fact, it is by making use of ^{19}F NMR with hypercoordinate silicon complexes³⁵ that the relative apicophilicities and pseudorotation energies^{78, 82b, 146} are obtained.

^{31}P NMR is also valuable when interactions of the type of $P=O \rightarrow Si$ are involved. The chemical shifts of ^{31}P of HMPA and Ph_3PO is reported 3~9 ppm downfield shifted upon coordination relative to the free base^{5, 147}.

1.5.3 DNMR in the study of reaction mechanisms

Dynamic NMR (DNMR) is an application of NMR spectroscopy employed to examine the changes in NMR spectra arising from a chemical exchange process¹³⁸. Conversely, the NMR spectra provide direct information about the change in the environment of the magnetic nuclei, which is due to the exchange between sites with different chemical shifts and/or different coupling constants.

The line shape of an NMR signal is related to the life time of the species under examination, which can be expressed by the Heisenberg Uncertainty Principle (Equation 1.4). Δt , the necessary time to pick up or record the signal, is governed by

$$\Delta t \cdot \Delta \nu = 1 / 2\pi$$

Equation 1.4

the rate constant as well as the Larmor frequency and spin-spin transverse relaxation time (T_2). Thus, slow rates (long life time) lead to separate NMR signals and fast rates cause overlapped or coalesced signals.

Spectroscopically, the bandshape of an NMR signal is determined by parameters such as the chemical shifts of each exchanging magnetic environment or sites (ν_i), the coupling constants (J), the population of each site (P_i) and the natural line width (W_i) which is related to T_2 .

Consider a two-spin system where nucleus A is undergoing chemical exchange with nucleus B with chemical shifts ν_A and ν_B and linewidths W_A and W_B respectively. A slight line broadening of each species is observed at a slow exchange rate, the broadening become much pronounced as the rates increase until the two signals merge and coalesce. Further increase of the exchange rate results in a new gradually sharpening signal until it eventually comes to an averaged signal with its natural line width. The chemical shift of the new signal is controlled by the relative populations (P_A , P_B) and the position (ν_A , ν_B) of the two exchanging species, as demonstrated in Equation 1.5 and 1.6. It is worth noticing that unequal populations of them will cause

$$\nu_{\text{observed}} = \nu_A P_A + \nu_B P_B \quad \text{Equation 1.5}$$

$$P_A + P_B = 1 \quad \text{Equation 1.6}$$

the less intense signal to broaden more quickly and to shift more strongly by exchange¹³⁸. With equal population, the changes are in a symmetric manner, as illustrated in Figure 1.13 (calculated bandshapes for an uncoupled , two site exchange system, $P_A = P_B$, $T_2 = 0.2$, $\delta_\nu = 600$ Hz, scaled to the height of the reference peak C).

Total line shape analysis enables rate constants as well as activation parameters to be determined for the full range of line shapes. Computer programs are available to suit specific requirements¹³⁸. However, the mathematical basis of the theory is complex

and will not be discussed here. DNMR has found its way successfully into the study of reaction mechanisms of organic silicon. It is the routine way of examining the formation of silane-nucleophile adducts and their kinetics in our laboratory^{51, 53}. Holmes¹⁴⁸ used it in his study of pentacoordinated ionic silicates. Corriu^{82b, 105} employed it not only in coordination chemistry of silicon but also in the reaction pathways. It may be said that the advance of the theories of the nucleophilic reactions of silicon in the past decades is based on the continued development of the NMR technique.

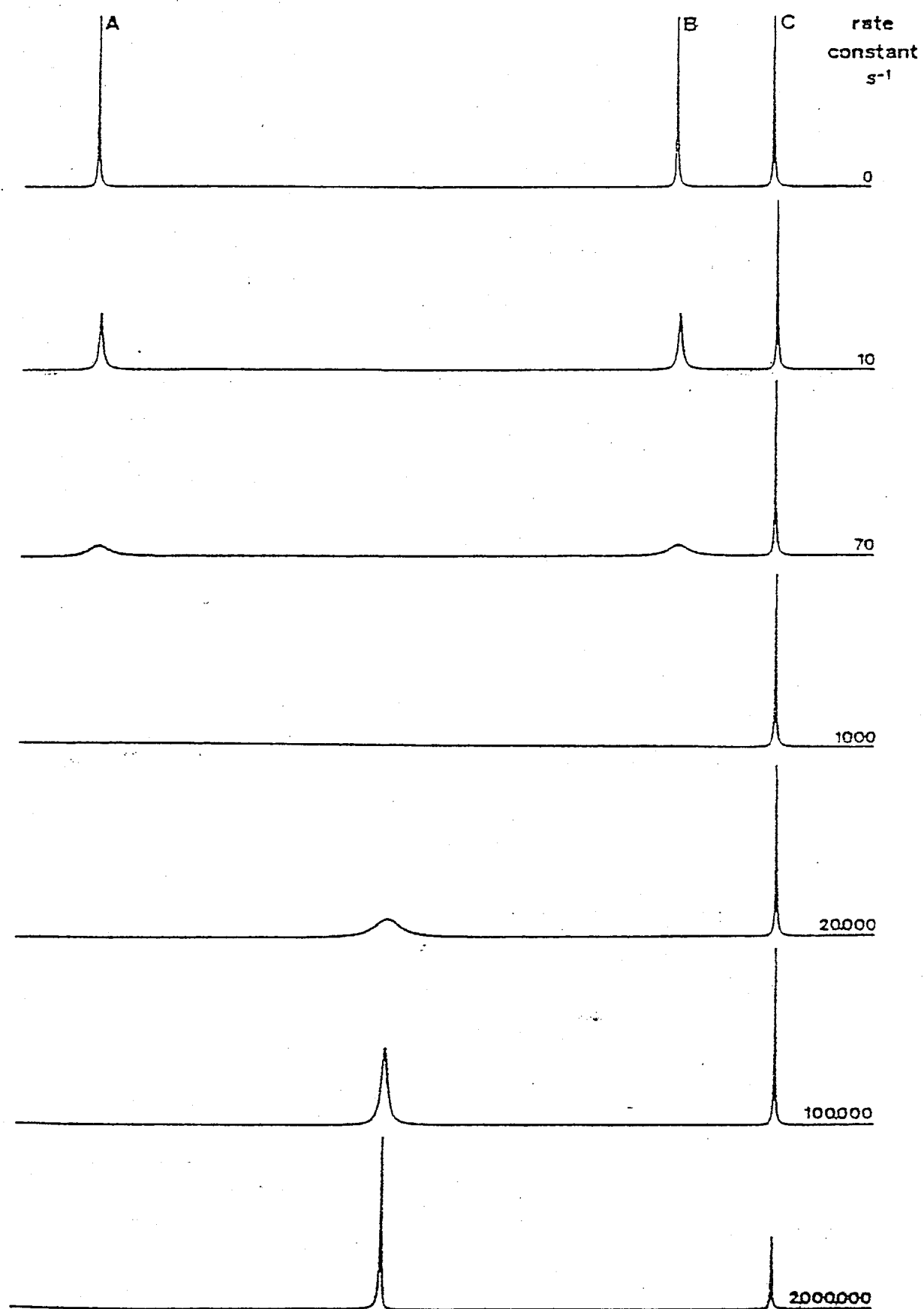
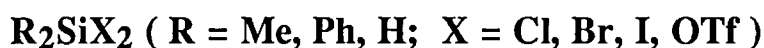


Figure 1.13 Line broadening of NMR signals.

Chapter 2 Interactions of nucleophiles with



2.1 Introduction

The key step in nucleophilic reaction mechanisms at silicon is frequently the formation of an extra coordinated intermediate or transition state. A number of pathways have been proposed, with intermediates ranging from four-coordinated ionic species to five- or six-coordinated complexes of which some have been isolated and identified experimentally. However, most of the hypercoordinate interpretations arose from comparison with cyclic or intramolecular coordinate systems, which have an extra entropic contribution. Relatively little has been done with simple, acyclic systems, which are the most important compounds in industry as well as in academia, and the results are diverse and controversial.

The monofunctional silane series R_3SiX is the most detailed studied of the simple, acyclic silanes. Chojnowski⁵ first suggested the formation of a tetracoordinate ionic intermediate, which was substantially supported by Bassindale *et al*^{51, 53, 98~100}. There is only slight evidence to verify the hypercoordinate pathways of R_3SiX . It is

reported that pentacoordinate cyanosilicate $\text{Bu}_4\text{N}^+\text{Me}_3\text{Si}(\text{CN})_2^-$ was easily formed and was observed in solution¹⁴⁹ whilst the formation of hexacoordinate fluorosilicate $(\text{Me}_4\text{N})_2^+\text{Me}_3\text{SiF}_3^{2-}$ needed severe conditions³⁸. Nonetheless, when $\text{R}=\text{H}$, R_3SiX displays a readiness to expand its coordination. Bassindale and co-workers^{51, 53, 102} found that $\text{R}'_2\text{HSiX}$ ($\text{R}' = \text{Ph}, \text{Me}$) formed pentacoordinate adducts with NMI, DMF and DMAP.

For the difunctional silane series R_2SiX_2 , the nucleophilic substitution reactions may proceed through pentacoordinate intermediates, such as R_2SiF_3^- ^{146b}. But Frye² strongly argued that it was the tetracoordinated ionic species acting as the key intermediate in alcoholysis of Ph_2SiX_2 . The mechanism of nucleophilic attack at difunctional silanes is still open to question. It is the aim of this chapter to establish possible reaction pathways of bifunctional silane with neutral nucleophiles in solution by examination of the interactions between R_2SiX_2 ($\text{R} = \text{Me}, \text{Ph}, \text{H}; \text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OTf}$) and nucleophiles ($\text{NMI}, \text{DMAP}, \text{HMPA}, \text{DMF}, \text{DMPU}$).

Method

NMR was chosen as the main analytical method to monitor the course of the reactions as well as to identify the species present in the reaction mixture. The reactions were carried out at room temperature in dry and nitrogen-flushed 10 mm NMR tubes unless specified otherwise. CDCl_3 , CD_3CN (and sometimes a mixture of them, which has been found to be a powerful solvent mixture in this study), were used as solvents, as there were problems of solubility of the adducts in some cases. The reaction process was controlled by titration of silanes against nucleophiles or vice versa. The NMR spectra, especially ^{29}Si NMR, were recorded when the temperature of the sample returned to room temperature, as all of the reactions between silane and nucleophiles were exothermic. A number of variable temperature NMR spectra were run with selected systems by lowering the temperature or warming the sample. The reaction equilibria and the coordinated adducts of the silanes were detected and interpreted according to the changes of the chemical shifts and line shapes.

In supporting the NMR results, conductivity measurements of the reacting system were performed in solutions of CHCl_3 , CH_3CN or mixture of them in a specially designed conductivity cell, which was airtight but allowed liquid to be injected in. The conductivity of the solution was read progressively when the silane was titrated with a nucleophile or vice versa. Sharp increases of the conductivity of the mixture indicate the formation of separated ionic species while small increases may be contributed to interactions between the solvents and solutes, low equilibrium concentrations (small K) or even the formation of tight ion pairs⁹⁹.

It was not considered necessary to isolate and then characterize all the various nucleophile-silane adducts, as this study concentrated particularly on solution state structures. However, in cases where solid adducts deposited, they were separated from the liquid and were subjected to elemental analysis in addition to solution NMR study if they could be re-dissolved. Mass spectrometry was employed unsuccessfully as there were problems of solubility and hydrolysis of the solids. Crystallization of the solids suitable for X-ray analysis was not achieved. Nonetheless the data of elemental microanalysis of the solid adducts are good collateral evidence of the adduct structure in solution.

The subsequent discussion is divided into three sub-sections, each dealing with a particular class of silanes interacting with neutral nucleophiles:

- (i) Me_2SiX_2 ;
- (ii) Ph_2SiCl_2 and PhMeSiCl_2 ;
- (iii) RHSiX_2 ($\text{R} = \text{Me}, \text{Ph}$).

2.2 The interaction of Me_2SiX_2 with nucleophiles

As has been stated in Chapter 1, the reaction mechanisms and stereochemistry of silanes are very much related to the leaving groups, X, in the case of Me_2SiX_2 . A number of different leaving groups including Cl, Br, I and OTf are to be investigated in

this subsection with selected nucleophiles.

2.2.1 The interactions of Me_2SiCl_2 with nucleophiles

Chlorosilanes R_3SiCl have been found to have very low equilibrium constants when they are reacting with neutral nucleophiles^{6, 51, 99, 100}. However in the examination of the interactions of dimethyldichlorosilane with nucleophiles in solution the problem of insolubility of the adducts in solvents was encountered. For example, the addition of Me_2SiCl_2 to NMI or vice versa in polar or nonpolar solvents such as C_6H_{14} , CH_2Cl_2 , CHCl_3 , CH_3CN and CH_3NO_2 resulted in either solids or emulsions immediately, or after a period of time. Similar phenomena covered nearly all reactions of multifunctional silanes with organic nucleophiles, which has, in the past, inhibited the study of the reaction to be investigated in solution in more detail. This problem remains in this study but reactions were made suitable for NMR and conductivity studies by trying many solvents or solvent mixtures or taking advantage of the time needed for the solids to deposit, The solvents are referenced in individual reactions.

The change of ^{29}Si chemical shifts indicates an alteration of the environment surrounding the silicon atom. Being a good electron acceptor, silicon is subject to nucleophilic attack. However, the increase of ^{29}Si chemical shift of Me_2SiCl_2 by nearly 2 ppm when CDCl_3 ($\delta^{29}\text{Si} = 32.15$) was replaced by CD_3CN ($\delta^{29}\text{Si} = 34.12$) as solvent can not be attributed to such donor-acceptor interactions as the latter is a relatively stronger nucleophile, but may arise from their dielectric constants (4.8 and 38.0 respectively). This means the nucleophilic reaction between Me_2SiCl_2 and very weak nucleophiles (solvents) can be ignored in the study¹³⁶.

The interaction of Me_2SiCl_2 and selected nucleophiles in solution was carried out successfully and was examined by ^{29}Si NMR in detail. The titrations of dimethyldichlorosilane with N-methylimidazole (NMI), hexamethylphosphoramide (HMPA) in acetonitrile- d_3 , N,N-dimethylformamide (DMF) in chloroform- d and N,N-dimethylaminopyridine (DMAP) in mixtures of acetonitrile- d_3 and chloroform- d

are shown in Figure 2.1.

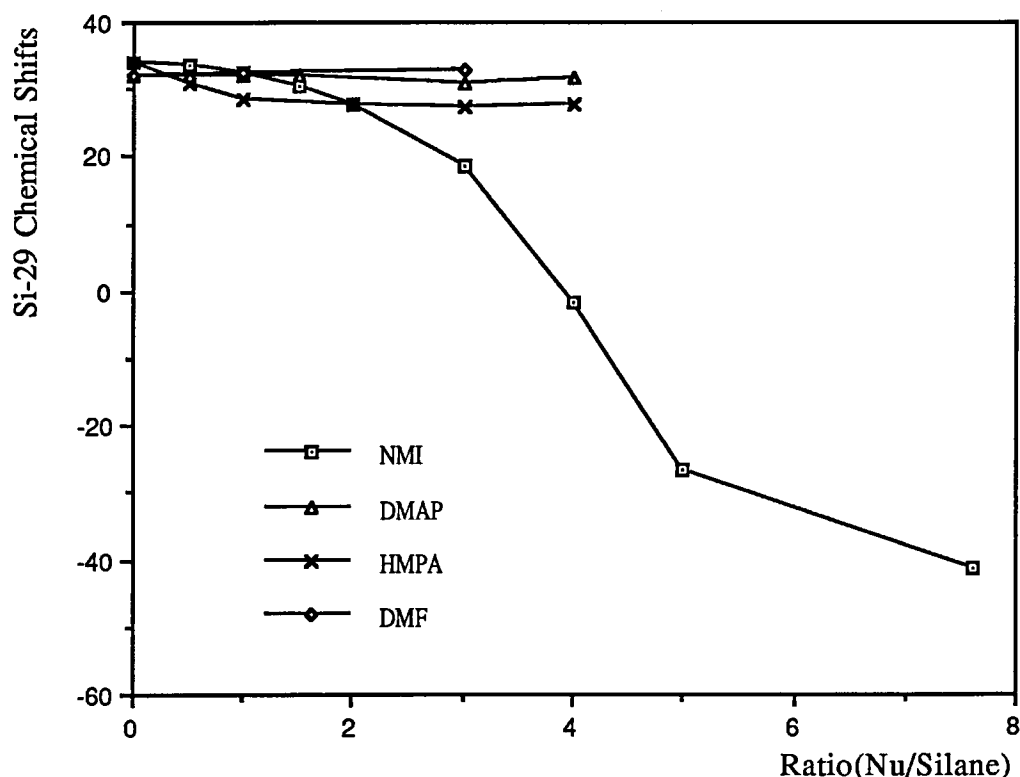


Figure 2.1 ^{29}Si chemical shifts titration of Me_2SiCl_2 with nucleophiles.

* Chemical shift values (ppm) of ^{29}Si , ^{13}C and ^1H are relative to TMS at 300K hereinafter unless specified otherwise;

** The concentrations quoted are related to the silane in the starting solution in mmol./ml unless specified otherwise;

*** $c = 1.22$ for NMI/silane in CD_3CN ; $c = 0.82$ for DMAP/silane and HMPA/silane in CDCl_3 and CD_3CN respectively; $c = 2.04$ for DMF/silane in CDCl_3 .

$\text{Me}_2\text{SiCl}_2 + \text{DMF}$ (or DMAP)

The addition of DMF into Me_2SiCl_2 in CDCl_3 up to three molar equivalents to the silane (r , molar ratio, which is used hereinafter unless specified otherwise) left the ^{29}Si chemical shift practically unchanged. The signal remained similar in its size and shape. In the case of DMAP, the change in chemical shift of the sharp signals of silicon-29 was less than 1 (0.6) ppm up to a four-fold excess of DMAP. The little

changed $\delta^{29}\text{Si}$ values of the silicon moieties suggest no significant reactions were taking place in these mixtures.

$\text{Me}_2\text{SiCl}_2 + \text{NMI}$ (or HMPA)

By contrast, the successive addition of NMI into Me_2SiCl_2 in CD_3CN made the ^{29}Si resonance shift strongly upfield; 74.9 ppm difference at a ratio of 7.56 molar equivalents of NMI, with the signals progressively broadening and diminishing. The addition of HMPA caused 6.4 ppm high field shift at a HMPA/silane ratio of four with signals remaining sharp. The high field shifts of ^{29}Si resonances show that there were nucleophilic interactions between the silane and the nucleophiles. For HMPA, at low concentration, the reaction was noticeable as there was a fast drop of ^{29}Si chemical shift. When more than two molar equivalents HMPA were present the $\delta^{29}\text{Si}$ value remained constant. The reaction could be either association or substitution by the nucleophile but the equilibrium remains substantially to the left. Subsequent experiments suggest substitution (see later). In the case of NMI, a $\delta^{29}\text{Si}$ value of -68 ppm was observed when neat NMI was used as solvent. The pronounced high field shift is large enough to suggest the formation of pentacoordinate adducts in equilibria.

$\text{Me}_2\text{SiCl}_2 + \text{Nu}$ at low temperature

In order to understand the effect of temperature on such interactions, variable temperature studies were carried out with the mixture of Me_2SiCl_2 and nucleophiles in solution. Some typical results of ^{29}Si chemical shifts at room and low temperatures are shown in Table 2.1.

The data in Table 2.1 show that weak nucleophiles such as DMF and DMPU do not react with Me_2SiCl_2 with any significance as the ^{29}Si chemical shifts stay nearly unchanged. The small high frequency shifts (0.05~0.22 ppm) are insignificant.

Strong nucleophiles such as NMI, HMPA and DMAP with the ^{29}Si resonance of the mixtures moved to high field by 26 to 33 ppm upon decreases of temperature about

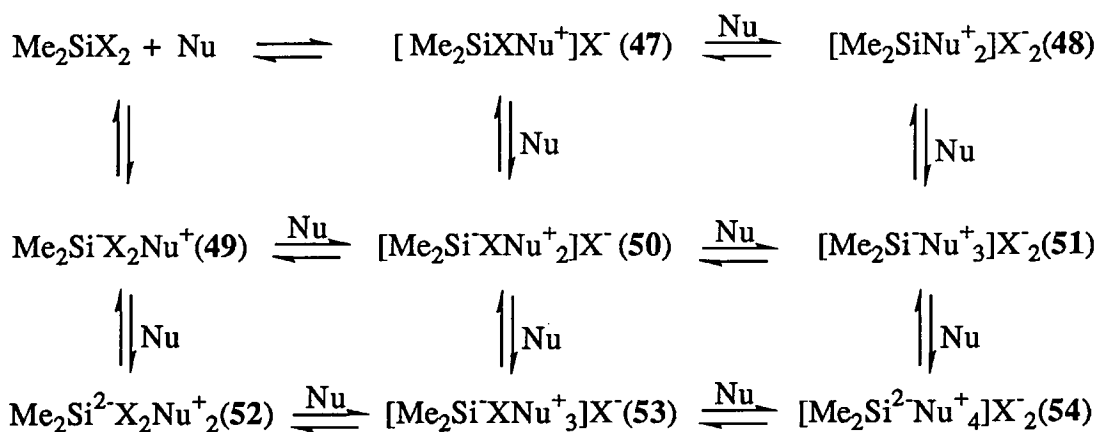
Table 2.1 $\delta^{29}\text{Si}$ of $\text{Me}_2\text{SiCl}_2 + r \text{ Nu}$ solutions at different temperatures.

Nu	r (Nu/silane)	c (silane) (mmol./ml)	Solvents	$\delta^{29}\text{Si}$ at 300(K).	$\delta^{29}\text{Si}$ at low temp. (low temp. K)**
NMI	7.6	0.6	CD_3CN	-41.20(br*)	-74.40 (sbr)(223)
HMPA	4.0	0.6	CD_3CN	27.76(sh)	2.08 (sbr)(235)
DMAP	4.2	0.1	$\text{CD}_3\text{CN}+\text{CDCl}_3$	32.20(sh)	6.03(sh)(220)
DMF	3.0	1.2	CDCl_3	32.92(sh)	32.97 (sh)(220)
DMPU	5.0	1.1	$\text{CD}_3\text{CN}+\text{CDCl}_3$	33.30(sh)	33.52 (sh)(228)

* sh or unmarked, sharp; sbr, slightly broadened; br, broadened hereinafter unless specified;

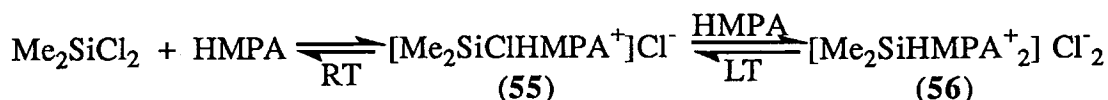
** The low temperatures listed were the lowest the samples were able to reach without solid formation.

65~80 K. The remarkable high field shifted $\delta^{29}\text{Si}$ values indicated that the nucleophilic interaction took place with the formation of silane-nucleophile adducts. However the equilibria of difunctional silane Me_2SiX_2 with nucleophiles Nu can take many forms, either by expansion of coordination or simple substitution, as shown in Scheme 2.1. The possible adducts **47** and **48** are tetracoordinate and **49**, **50** and **51** are pentacoordinate whilst **52**, **53** and **54** are hexacoordinate. In a complex set of reactions such as these it may be impossible to determine separately the chemical shifts of each of the species. In the systems of Me_2SiCl_2 with DMAP and HMPA, the $\delta^{29}\text{Si}$ values of 6.03, 2.08 ppm respectively, and the nearly unchanged bandshapes of the signals at low temperature strongly suggest formation of tetracoordinate silicon species, though the existence of fast exchange with hypercoordinated complexes can not be ruled out yet. Actually, as will be proved later on, the interactions of HMPA

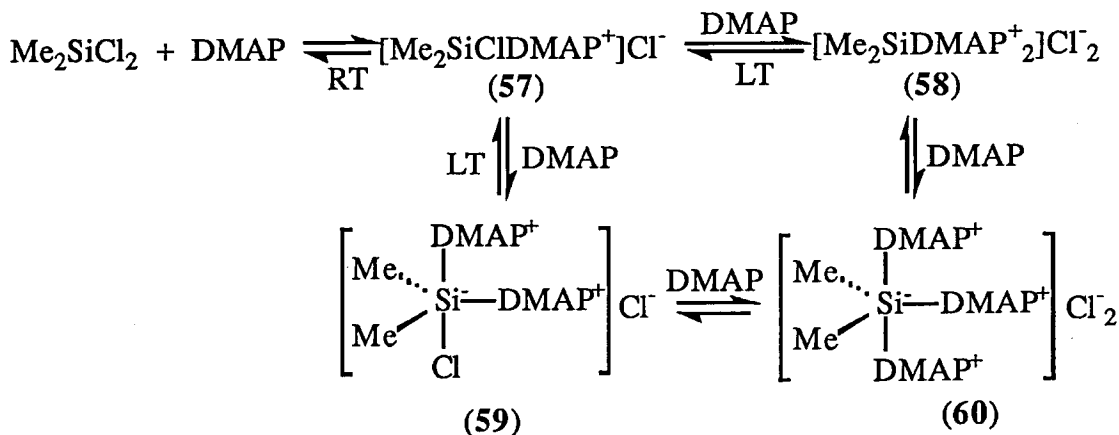


Scheme 2.1 Possible interaction equilibria of Me_2SiX_2 with nucleophiles.

and DMAP can be described in the following equations (RT = room temperature, LT = low temperature hereinafter unless specified otherwise):



Equation 2.1



Equation 2.2

Variable temperature study of Me_2SiCl_2 + 7.6 NMI

The large high field shift of the Me_2SiCl_2 -NMI mixture to -74.4 ppm at 223 K with 108.5 ppm difference from that of Me_2SiCl_2 results from the formation of a

pentacoordinate complex or the possible existence of equilibria among tetra- and penta- and hexa-coordinate species. Variable temperature study of this mixture demonstrates a rather smooth curve, see Figure 2.2, with signals increasing sizes

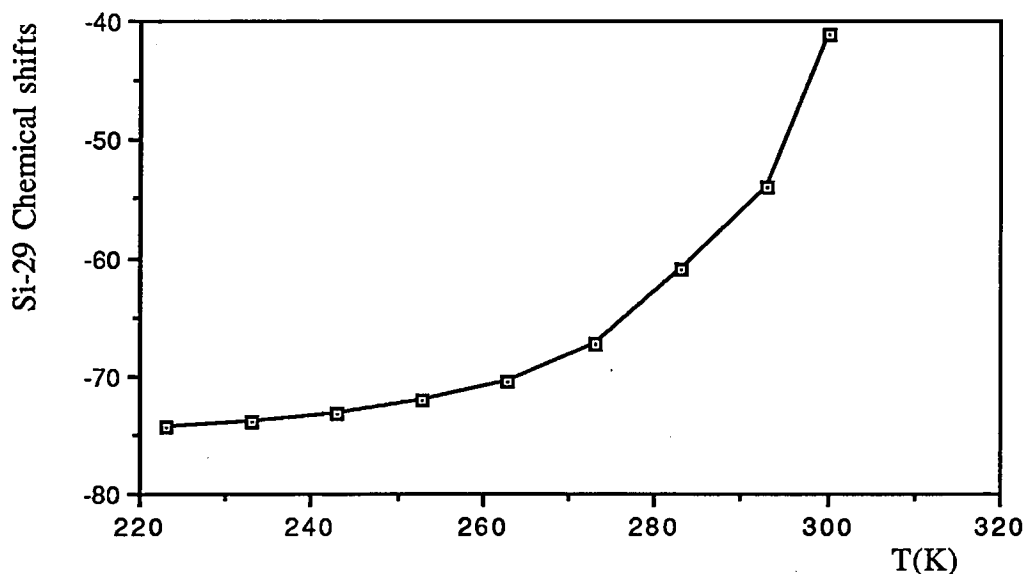


Figure 2.2 Variable temperature study of $\text{Me}_2\text{SiCl}_2 + 7.6 \text{ NMI}$.

$c = 0.60 \text{ mmol./ml}$ in CD_3CN .

and less broadening as the temperature decreases. This means, most likely, that it is tetra- and penta-coordinate adducts that are present in the main.

Conductivity studies of $\text{Me}_2\text{SiCl}_2 + \text{Nu}$

The formation of the complexes shown in Scheme 2.1 will result in an alteration of electrical conductive property of the solution. Intramolecular ionic pairs **49** and **52** will have no contribution to the conductivity of the solution and those intermolecular ionic pairs, which may be dissociated into separated ions by solvation, are responsible for the increases of conductivity of the solution. Conductivity studies, see Figure 2.3, show the mixing of Me_2SiCl_2 and NMI increases the conductivity of the solution enormously. It is notable that when NMI is being added to Me_2SiCl_2 the conductivities of the the solution increase gradually while titrating NMI with

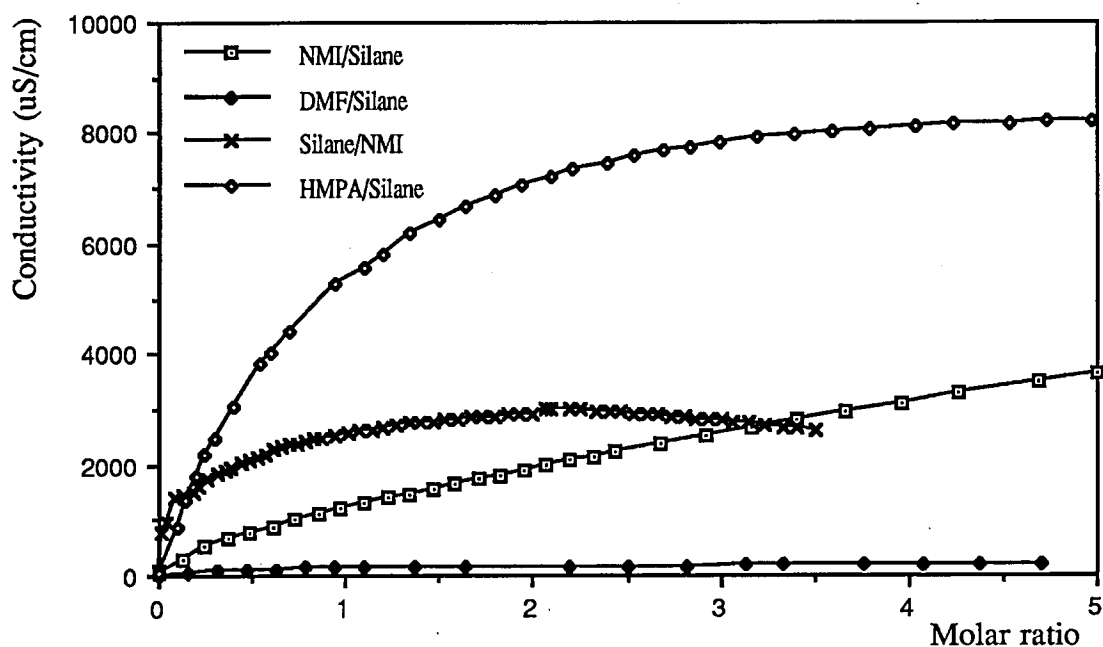


Figure 2.3 Conductivity titration of Me_2SiCl_2 and nucleophiles in CH_3CN .

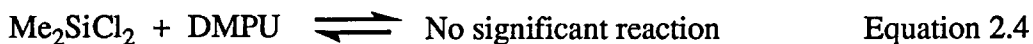
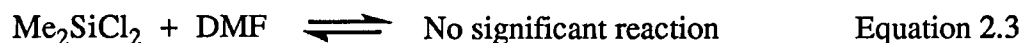
NMI against Me_2SiCl_2 , $c = 0.63 \text{ mmol./ml}$; Me_2SiCl_2 against NMI, $c = 0.34 \text{ mmol./ml}$;

DMF against Me_2SiCl_2 , $c = 0.14 \text{ mmol./ml}$; HMPA against Me_2SiCl_2 , $c = 0.55 \text{ mmol./ml}$.

Me_2SiCl_2 the increases come largely at the beginning, eg. at low concentration of Me_2SiCl_2 , and decrease slowly after it reaches the highest point at about $r=2$. Similar phenomena were observed with Me_2SiCl_2 and HMPA. These mean that the interaction of strong neutral nucleophiles with Me_2SiCl_2 produces ionic adducts and the complexes **49**, **52** from direct coordinate a nucleophile to silicon are very unlikely to be existing in any significant quantity.

In contrast to the strong nucleophiles, weak nucleophiles such as DMF, just produced slight increases in the conductivities of the solutions whether they were added to Me_2SiCl_2 or vice versa. This agrees with the ^{29}Si NMR results that there is little interaction in the mixtures. The small increase of conductivity may be caused by the formation of very small amounts of adducts, or in extreme cases, the partial hydrolysis of the silane. Whatever the reason is, this verified the formation of ionic species with strong nucleophile systems.

The interactions of weak nucleophiles DMF and DMPU with Me_2SiCl_2 can be expressed as follows:

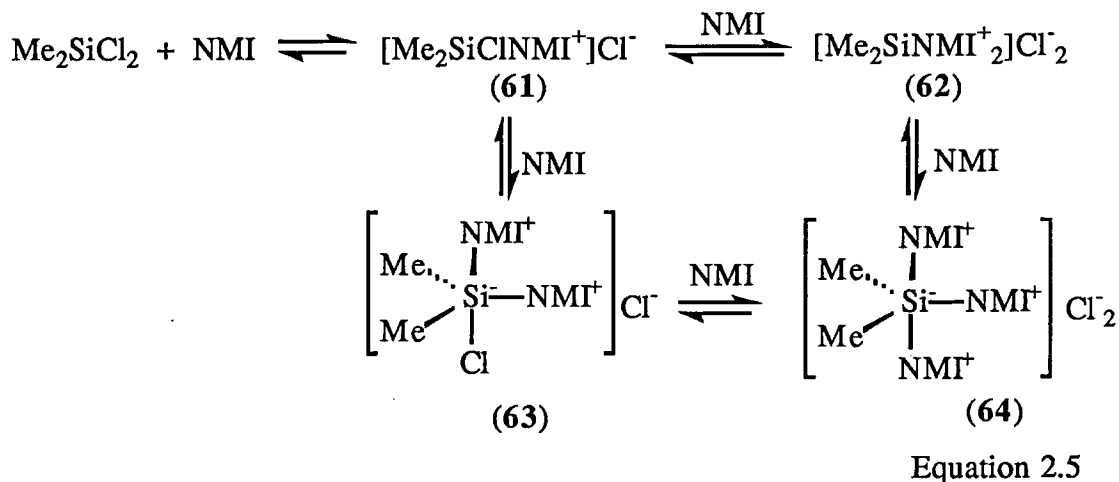


Solid adducts

Efforts were made to separate and identify the solids precipitated in the reacting mixtures. The solids were obtained from Me_2SiCl_2 and NMI in six occasions from either CH_3CN or CH_2Cl_2 . The chemical shifts of ^{29}Si and ^1H after they were re-dissolved in solvents are concentration dependent. $\delta^{29}\text{Si}$ values from 4.1 to 32.0 ppm were recorded. Integration measurements of the proton signals showed the ratio between Me_2SiCl_2 and NMI to be about 1:2. Elemental analysis confirmed these results. This means the solid adducts directly formed from the the reaction mixture are one molecular silane combined to two NMI molecules. However, recrystallization of the solids under vacuum by evaporation (0.05 mmHg, 50°C) increased the number of NMI co-deposited with Me_2SiCl_2 to about four (measured by ^1H NMR integration in CDCl_3 , $\delta^{29}\text{Si} = -47.5$ ppm). This agrees with Hensen's results^{52a}, see complex 9, and indicates the structure of solid adducts of Me_2SiCl_2 and NMI can take different forms, which may also exist in solution. That is to say nucleophiles such as NMI reacting with Me_2SiCl_2 in solution may first mono- or double displace chlorine groups and subsequently add an extra nucleophile to form a pentacoordinate complex if the nucleophile is strong enough. Therefore the interaction of Me_2SiCl_2 with NMI can be summarized in Equation 2.5.

2.2.2 The interaction of Me_2SiBr_2 with nucleophiles

The interactions of Me_2SiBr_2 with nucleophiles were more exothermic, on the whole,



than those of Me_2SiCl_2 . Considering that the Si-Br bond has a lower dissociation energy than Si-Cl bond and Br is a better leaving group, it is conceivable that Me_2SiBr_2 takes the same pathway as Me_2SiCl_2 does but with a higher reactivity when it reacts with similar nucleophiles.

$\text{Me}_2\text{SiBr}_2 + \text{NMI}$ (or DMAP)

The reactions of Me_2SiBr_2 with strong nucleophiles such as NMI and DMAP produced solid adducts more readily than Me_2SiCl_2 . Actually, any addition of NMI or DMAP into Me_2SiBr_2 in various solvents resulted in precipitates immediately. However NMR signals were observed by adding Me_2SiBr_2 into NMI or DMAP in a mixed solvent of CD_3CN and CDCl_3 at very low concentration (0.015~0.20 mmol./ml), see Table 2.2. Like those of Me_2SiCl_2 and NMI, ^{29}Si NMR resonances of the mixtures of Me_2SiBr_2 and NMI shifted significantly high field to about -70 ppm, which indicated the formation of a pentacoordinate complex. In contrast, the $\delta^{29}\text{Si}$ value of the mixture of Me_2SiBr_2 with a six molar equivalents of DMAP just shifted to high field by 2.5 ppm. However, the protons of the methyl groups bonded to silicon were notably shifted to low field (0.2~0.32 ppm) in both cases. The increased deshielding of the protons may be attributed to the equilibria between Me_2SiBr_2 and its adducts.

Low temperature studies, see Figure 2.4, show that the ^{29}Si resonances of the

Table 2.2. NMR data for mixture of $\text{Me}_2\text{SiBr}_2 + r \text{ Nu}$ in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

	r	with NMI	$\Delta\delta^*$	with DMAP	$\Delta\delta$
$\delta^{29}\text{Si}$	in NMI	-70.4	-92.4		
$\delta^{29}\text{Si}$	19	-67.4(sbr)	-89.4		
$\delta^1\text{H}(\text{SiMe})$		1.32	0.20		
$\delta^{29}\text{Si}$	6	-63.5(sbr)	-85.5	19.5(sbr)	2.5
$\delta^1\text{H}(\text{SiMe})$		1.35(sbr)	0.23	1.44(br)	0.32
	5	solids		solids	

* $\Delta\delta = \delta_{\text{adducts}} - \delta_{\text{reactants}}$, hereinafter unless specified otherwise.

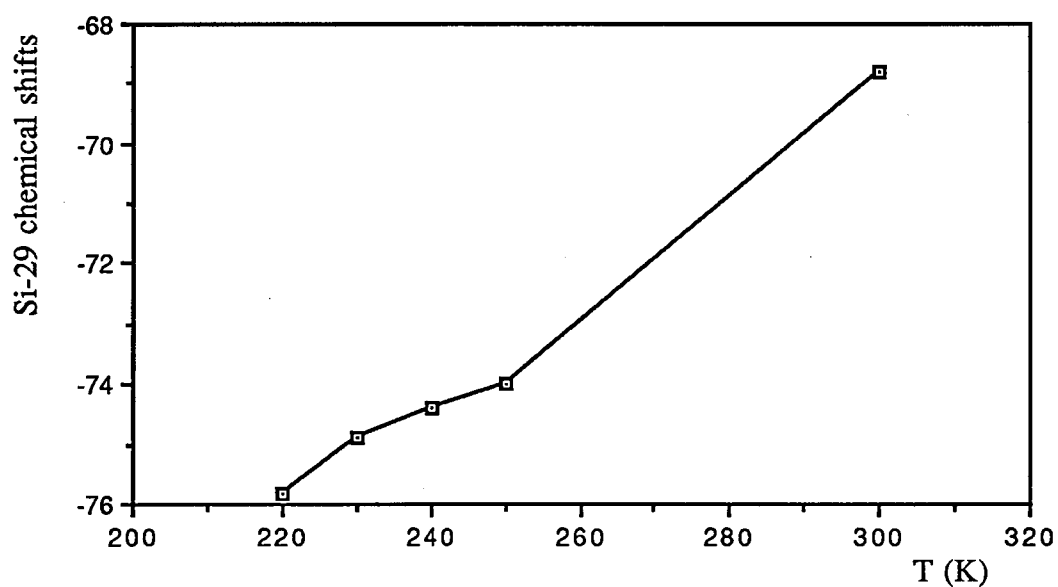
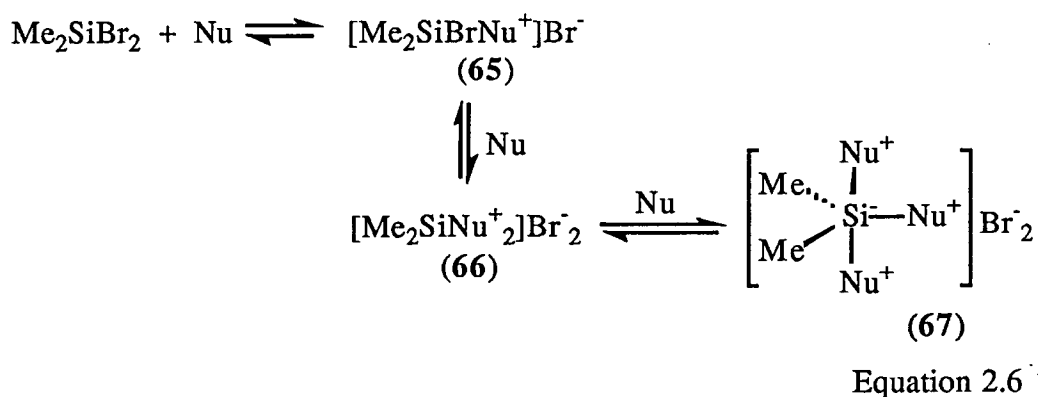


Figure 2.4 Variable temperature study of the mixture of $\text{Me}_2\text{SiBr}_2 + 18.1\text{NMI}$

Solvent, $\text{CD}_3\text{CN} + \text{CDCl}_3$; $c = 0.20 \text{ mmol.ml}^{-1}$ for Me_2SiBr_2 .

mixture of Me_2SiBr_2 with DMAP had a null signal at 240 K while the one with NMI moved slightly towards high field as the temperature was lowered gradually. The signal at 220K is nearly natural width, though a null signal was also recorded at 270K. This suggests that the equilibrium between a penta- and tetra-coordinate species dominates the interaction of Me_2SiBr_2 and NMI at high NMI to silane ratios.

The interactions of Me_2SiBr_2 with NMI or DMAP in solution, as will be proved later on, are similar to those of Me_2SiCl_2 and can be expressed in Equation 2.6 (Nu = NMI and DMAP here).



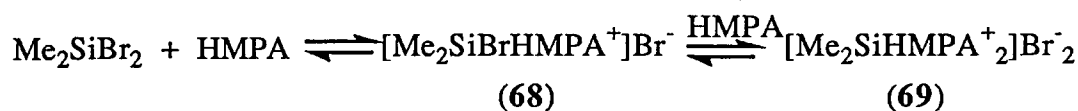
$\text{Me}_2\text{SiBr}_2 + \text{HMPA}$

The NMR properties of the mixture of HMPA with Me_2SiBr_2 were different, see Table 2.3. The addition of 0.9 molar equivalents of HMPA into Me_2SiBr_2 resulted in a highly broadened ^{29}Si signal at about 11.8 ppm. Although further addition of HMPA made the ^{29}Si resonance shift high field to around -2.5 ppm, that was the limiting value even at lower temperature or at a five equivalents of HMPA. The ^{29}Si chemical shift values demonstrate the adduct to be tetracoordinate. Interestingly, the resonance of the protons of the methyl groups attached to silicon, instead moving to low field as in the cases of NMI and DMAP, shifted high field upon complexing with HMPA. The high field shift with HMPA suggests that the electron density distribution around the protons is different from those caused by NMI and DMAP,

Table 2.3 NMR data for mixtures of Me₂SiBr₂ + r HMPA in CD₃CN + CDCl₃(c=0.2).

r	T (K)	δ ²⁹ Si	Δδ ²⁹ Si	δ ¹ H (SiMe)	Δδ ¹ H
0	300	22.00		1.12	
0.9	300	11.8(vbr)	-10.2	1.01	-0.11
3.0	300	-2.63(sh)	-24.6	0.95	-0.17
	250	-2.91	-24.9	0.94	-0.18
5.0	300	-2.56	-24.6	0.95	-0.17

which may be related to the inability of the tetracoordinate [Me₂SiHMPA⁺₂] adduct to coordinate further. Therefore the interaction of Me₂SiBr₂ with HMPA is just a substitution reaction without increase of the coordination number at silicon, as shown in Equation 2.7.



Equation 2.7

Me₂SiBr₂ + DMF (or DMPU)

The greater reactivity of Me₂SiBr₂ relative to Me₂SiCl₂ is also reflected in its reaction with weak nucleophiles, though the effect of solvents is similar to that of Me₂SiCl₂ and is insignificant (δ²⁹Si = 19.8 in CDCl₃ and 22.0 ppm in CD₃CN). The addition of weak nucleophiles such as DMPU and DMF into Me₂SiBr₂ in CDCl₃ pushed the chemical shifts of both ²⁹Si and ¹H away from those of Me₂SiBr₂, see Figure 2.5 &

2.6. The most striking change among them was with the interaction between Me_2SiBr_2 and DMF. The $\delta^{29}\text{Si}$ values shifted rapidly to high field with increasing broadening signals as DMF was injected successively; and reached -25.73 ppm at

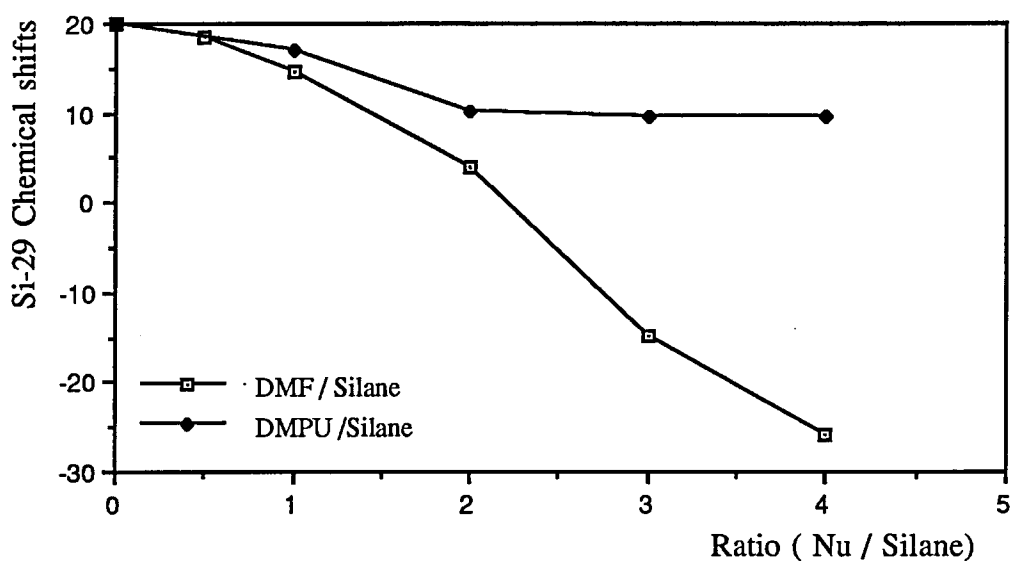


Figure 2.5 ^{29}Si chemical shifts titration of DMF and DMPU against Me_2SiBr_2

$c = 0.2$ for DMF/silane in $\text{CD}_3\text{CN} + \text{CDCl}_3$; $c = 1.2$ for DMPU in CDCl_3 .

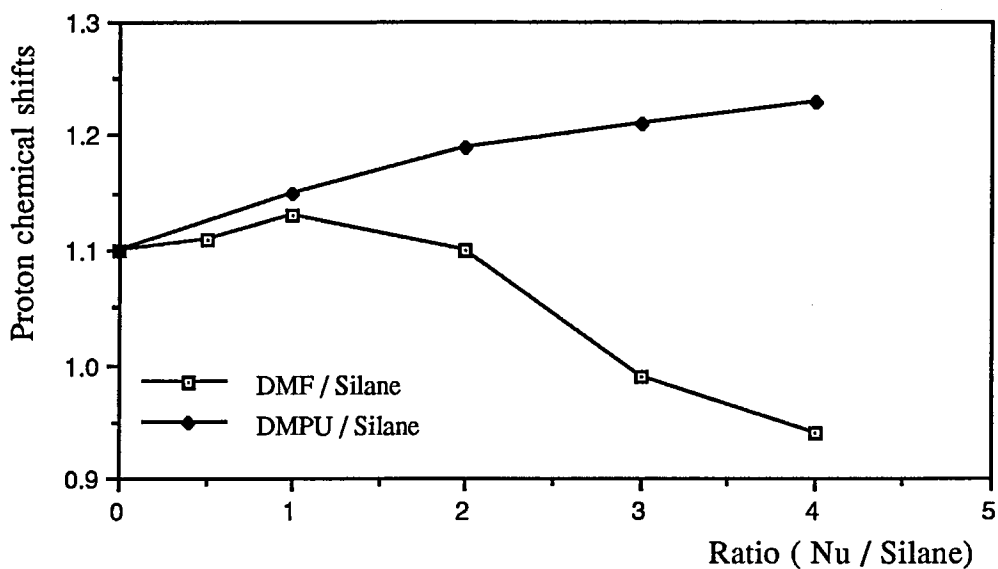


Figure 2.6 ^1H chemical shifts (MeSi) titration of DMF and DMPU against Me_2SiBr_2 .

$c = 0.2$ for DMF/silane in $\text{CD}_3\text{CN} + \text{CDCl}_3$; $c = 1.2$ for DMPU in CDCl_3 .

just a ratio of four DMF to the silane. The chemical shifts were concentration and temperature dependent. When the sample was diluted by 30%, the $\delta^{29}\text{Si}$ value moved from -25.73 to -21.61 ppm, but it shifted down to -46.63 ppm as the temperature was lowered to 250K. The trend of the ^{29}Si resonance, like that of Me_2SiBr_2 with NMI, points to the formation of a pentacoordinate adduct. Therefore Equation 2.6 can be expanded to include DMF. The ^{29}Si NMR signals of Me_2SiBr_2 with DMPU shifted slowly to low frequency with nearly natural width and stayed at about 9.0 ppm, showing the main species in the equilibrium to be tetracoordinated, like those of Me_2SiBr_2 with HMPA (Equation 2.7). However the proton signals of the methyl groups next to silicon shifted in opposite directions for NMI and DMF, and similarly opposite directions for HMPA and DMPU. Therefore, the proton chemical shifts of the silane moiety are more a diagnostic measurement of the electronic and steric properties of the functional groups (X or Nu) than a function of the coordination numbers at silicon atom.

Conductivity studies of $\text{Me}_2\text{SiBr}_2 + \text{Nu}$

The mixture of Me_2SiBr_2 and HMPA solution has great conductivity in CH_3CN . The titration curves showed two interesting inflexion points, as shown in Figure 2.7.

Titration of Me_2SiBr_2 with the addition of HMPA displayed an initial increase of conductivity and reached the maximal point at ratio about 2.2 while the titration of HMPA with adding Me_2SiBr_2 it changed sharply around a ratio of 0.6. These indicate that the interaction between HMPA and Me_2SiBr_2 produces ionic adducts with molar ratio 2:1 (see Equation 2.7) and the equilibrium has a large value for K, though not large enough to complete the reaction quantitatively at the exact ratio 2:1.

Conductivity titrations of DMF, DMPU and NMI with Me_2SiBr_2 showed similar phenomena, though the inflexion points were not so clearly distinguished as shown in Figure 2.8. The increases in conductivities were apparent immediately upon addition of Me_2SiBr_2 although the magnitude would be affected by the solvents and the

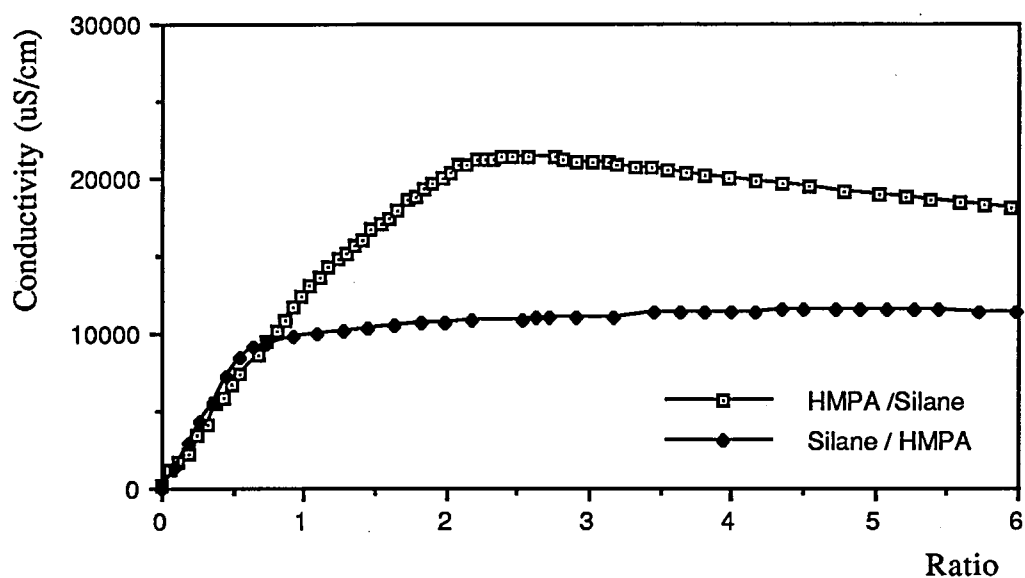


Figure 2.7 Conductivity titrations of Me_2SiBr_2 and HMPA in CH_3CN .

HMPA against Me_2SiBr_2 , $c = 0.16 \text{ mmol./ml}$; Me_2SiBr_2 against HMPA, $c = 0.14 \text{ mmol./ml}$.

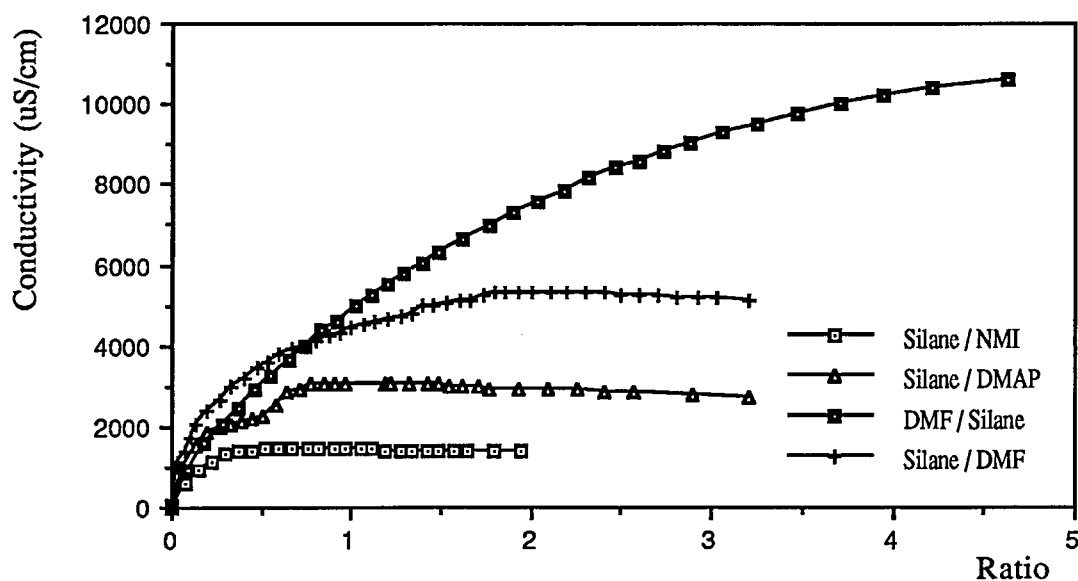


Figure 2.8 Conductivity titrations of Me_2SiBr_2 and nucleophiles.

Me_2SiBr_2 against NMI, $c = 0.17 \text{ mmol./ml}$, in $\text{CHCl}_3 + \text{CH}_3\text{CN}$; Me_2SiBr_2 against DMAP, $c = 0.4 \text{ mmol./ml}$, in $\text{CHCl}_3 + \text{CH}_3\text{CN}$; Me_2SiBr_2 against DMF, $c = 0.38 \text{ mmol./ml}$, in CH_3CN ; DMF against Me_2SiBr_2 , $c = 0.48 \text{ mmol./ml}$, in CH_3CN .

concentration of the reactants. The conductivity in the titration against NMI levelled off at ratio about 0.4 and against DMAP at about 0.8 with a light blue colour appearing

around 0.5 where the rate of increase in conductivity slowed. In the case of DMF, no definite point can be directly seen. These points of inflexion indicate the ability of a nucleophile to form ionic adducts with Me_2SiBr_2 . However, titration of Me_2SiBr_2 with DMF showed a steady increase of conductivity of the solution. NMI acted in the same way. The small changes in conductivity at high ratios suggest the reactions have gone to completion.

Solid adducts of $\text{Me}_2\text{SiBr}_2 + r \text{Nu}$

Solid adducts separated from the reactions of Me_2SiBr_2 with NMI, DMAP and DMF all have the formula of $\text{Me}_2\text{SiBr}_2\text{Nu}_2$, analyzed by elemental analysis. Because of the insolubility of the adducts, only $\text{Me}_2\text{SiBr}_2\text{NMI}_2$ has been confirmed by proton NMR integrations.

2.2.3 The interaction of Me_2SiI_2 with nucleophiles

The study of the interaction of Me_2SiI_2 with NMI in solution was difficult as the formation of solid adducts was pronounced. For example, Me_2SiI_2 with CD_3CN alone immediately produced a yellowish solid, which was soluble by addition of CDCl_3 and the chemical shifts of ^{29}Si , ^1H and ^{13}C were slightly deshielded (see Appendix 1).

$\text{Me}_2\text{SiI}_2 + \text{NMI}$

Titration of Me_2SiI_2 in dilute solution with NMI produced an upside down V-shape curve when the ^{29}Si resonances were plotted against molar ratio of NMI to silane, as shown in Figure 2.9.

A resonance at $\delta^{29}\text{Si} = -69.6$ ppm was also recorded using NMI as solvent. The chemical shifts of the mixture were concentration dependent as well. The initial increase of deshielding of ^{29}Si indicates the I groups were being replaced and the subsequent increase in shielding of ^{29}Si with broadening and diminishing signals is consistent with the equilibrium changing towards the pentacoordinate species formed by accepting an extra NMI.

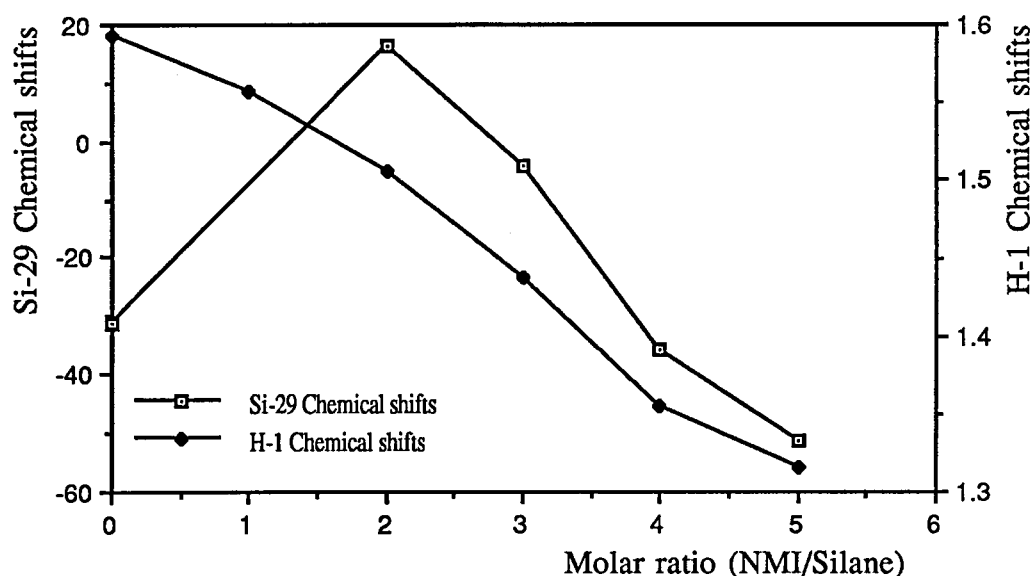


Figure 2.9 NMR titration of Me_2SiI_2 and NMI in $\text{CD}_3\text{CN} + \text{CDCl}_3$.
 $c = 0.078 \text{ mmol./ml}$ relative to Me_2SiI_2 ; ^1H NMR were those of the silane moiety.

The ^1H NMR of the methyl groups bonded to silicon became more and more shielded as NMI was added (see Figure 2.9). The high field shifts were similar to those of Me_2SiCl_2 and Me_2SiBr_2 with NMI (1.24 and 1.32 ppm respectively) and all approached a chemical shift value of 1.3 ppm.

A variable temperature study presents further evidence for the formation of a pentacoordinate adduct in the equilibrium. As the temperature of the sample became lower, the ^{29}Si resonance steadily shifted to high field, as shown in Figure 2.10.

The ^{29}Si value of -75.3 ppm at 220 K is almost the same as those of Me_2SiBr_2 and Me_2SiCl_2 with NMI at the same temperature (-75.8 and -74.4 ppm at ratios 18.1 and 7.6 respectively). The similarity of ^{29}Si and ^1H chemical shifts indicates that the interactions between Me_2SiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and NMI produce adducts with a similar structure in solution, that is the pentacoordinate complexes $[\text{Me}_2\text{Si}^-\text{Nu}^+_3]\text{X}^-_2$. Therefore the interaction of Me_2SiI_2 with NMI can be summarized similarly by Equation 2.8.

Solid separated from the mixture of Me_2SiI_2 and NMI was analysed by elemental microanalysis and displayed a formula of $\text{Me}_2\text{SiI}_2 \cdot 3\text{NMI}$.

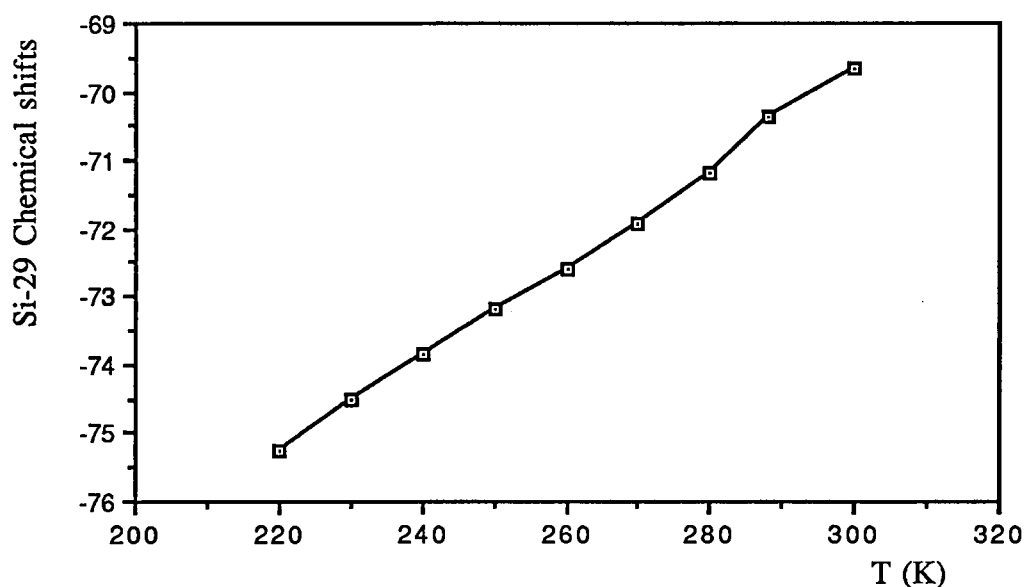
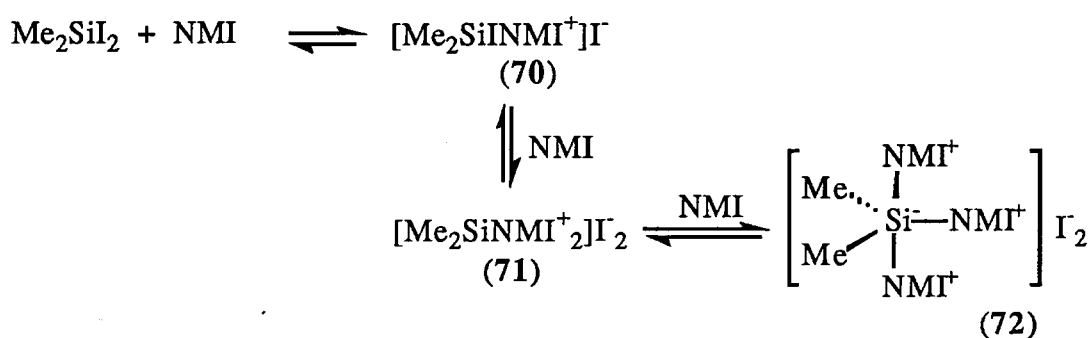


Figure 2.10 Variable temperature study of $\text{Me}_2\text{SiI}_2 + 8.9 \text{ NMI}$.

$c = 0.3 \text{ mmol./ml}$ in $\text{CD}_3\text{CN} + \text{CDCl}_3$.



Equation 2.8

$\text{Me}_2\text{SiI}_2 + \text{HMPA}$

The addition of HMPA to Me_2SiI_2 in CDCl_3 showed a very facile substitution reaction, but no evidence of pentacoordination was found (Table 2.4). There were two small and broadened ^{29}Si signals at -32.31 and -2.85 ppm when 0.9 molar equivalents of HMPA was added to Me_2SiI_2 . These two signals corresponded to intermediate exchange between the unreacted silane and tetracoordinate substituted adducts. Interestingly, when HMPA increased to 1.6 equivalents, a triplet around -2.9 ppm was recorded, which was in conformity to the coupling of one ^{29}Si atom with two

Table 2.4 NMR properties of the mixtures of $\text{Me}_2\text{SiI}_2 + r \text{ HMPA}$ in CDCl_3 .

	r	$\delta^{29}\text{Si}$	$\delta^{31}\text{P}$	$J_{\text{Si-P}}$	$\delta^{13}\text{C}$ (ppm)		$\delta^1\text{H}$ (ppm)	
		(ppm)	(ppm)		HMPA	Me_2Si	HMPA	Me_2Si
1	0.0	-33.52	(23.89)*		(36.82 36.65)	13.58	(2.68 2.59)	1.58
2	0.9	-32.31 (s**,br) -2.85(br)	26.05 25.10(s)		37.51	12.64(s) 8.67(s) 1.72	2.98 2.86	1.60(s) 1.21(s) 0.99
3	1.6***	-2.63 -2.91 -3.18	25.78 24.86(s)	4.9 4.9	37.68 37.46	1.67	3.01, 2.89 2.96(s) 2.84(s)	0.98 1.21 (s,br)
4	2.7	-2.85	26.25		37.34 37.11	1.32	2.86 2.75	0.92
5	2.7 ****	-3.18	26.11 (sbr)		36.94 36.77	0.80	2.82 2.71	0.89
6	5.0	-2.9						

* Chemical shifts for the nucleophile itself are recorded in the brackets for comparison;

$\delta^{31}\text{P}$ values relative to H_3PO_4 ; hereinafter unless specified otherwise.

** s, small size of the signal and hereinafter unless specified otherwise.

*** CD_3CN was added to make the sample free from emulsion.

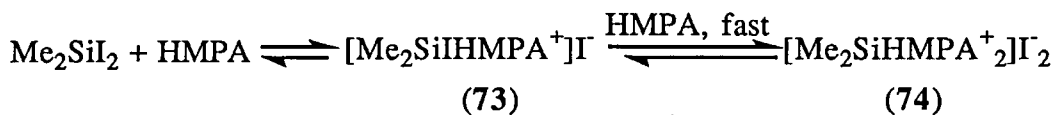
**** At 222 K.

^{31}P atoms with a coupling constant of 4.9 Hz. This indicated the two iodide ions were replaced by two equivalents of HMPA. The coupling disappeared with further addition of HMPA owing to the fast exchange between the excess free HMPA and the bonded HMPA. However, neither continued addition of HMPA nor lowering the temperature of the sample would alter significantly the position of the silicon-29 resonance. This can serve as proof that only double substituted adducts were formed in the interaction of HMPA with Me_2SiI_2 and the mono-substituted species was more reactive than Me_2SiI_2 as the equilibrium observed by ^{29}Si NMR was mainly between $[\text{Me}_2\text{SiHMPA}^+_2] \text{I}^-_2$ and Me_2SiI_2 .

The increased deshielding of ^{13}C , ^{31}P and ^1H of the nucleophile HMPA and the enhanced shielding of ^{13}C and ^1H of the Me_2Si moiety agree with a donor-acceptor type of interaction as the electron density shifted from the donor HMPA to the acceptor silane.

Although no signal of a mono-substituted species was seen by ^{29}Si NMR, there were signs of the existence of such an intermediate in small amount in the ^{31}P , ^{13}C and ^1H NMR spectra. In the ^{31}P spectra, there was a small signal around 25 ppm in addition to the main one at 26.05 ppm (see Entry 2, 3 of Table 2.4). The low field shifts suggested that they both were in complexed structures. In the ^{13}C spectrum (see Entry 2 of Table 2.4), there was also an additional minor peak at 8.67 ppm. Clearer evidence came from the proton spectra (see Entry 2 and 3 of Table 2.4), in which there was a small signal of Me_2Si at 1.21 ppm and a small doublet from an HMPA molecule at 2.96 and 2.84 ppm. All these weak signals of ^{13}C and ^1H were between those of the unreacted silane and the double substituted adducts. This observation demonstrated the existence in very small amounts of mono-substituted intermediate $[\text{Me}_2\text{SiI}(\text{HMPA}^+)] \text{I}^-$.

The interaction of Me_2SiI_2 with HMPA, therefore, can be described by Equation 2.9, similar to Equation 2.7.



Equation 2.9

Me₂SiI₂ + DMF

NMR studies of the interactions of Me₂SiI₂ with weaker nucleophiles, such as DMF and DMPU, have also showed that the mono-substituted adducts [Me₂SiNu⁺][−] were quite reactive. For the NMR data relating to the addition of 0.9 equivalents of DMF to Me₂SiI₂ in a mixture solvent, see Table 2.5, there were two broadened ²⁹Si signals, which indicated Me₂SiI₂ (-32.15 ppm) was exchanging at an intermediate

Table 2.5 NMR data of the mixtures of Me₂SiI₂ + r DMF in CD₃CN + CDCl₃.

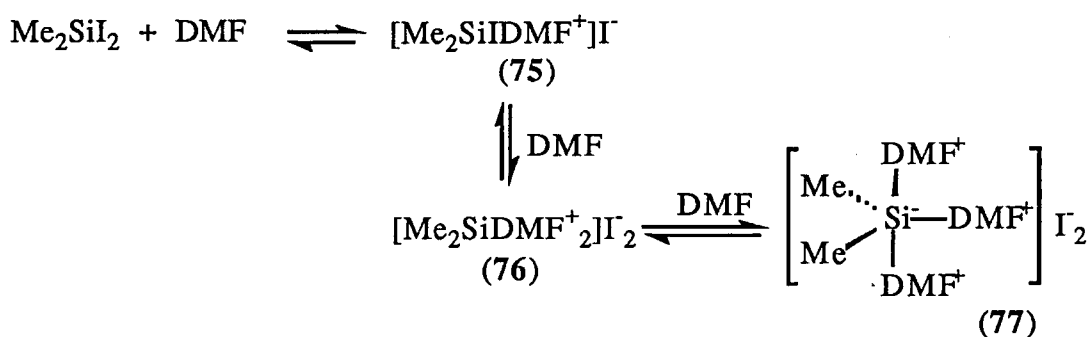
r	δ ²⁹ Si* (ppm)	δ ¹³ C (ppm)		δ ¹ H (ppm)	
		DMF	Me ₂ Si	DMF	Me ₂ Si
0.0	-31.27	(162.52, 36.31, 31.14)	13.27	(8.00, 3.98, 2.84)	1.58
0.9	-32.15(br) 19.48(br)	162.00, 42.22, 38.09	12.75(vbr)	9.21,3.57, 3.33, 3.31	1.41~1.27 (vbr)
7.1*	-37.56	163.26, 37.40, , 32.17	3.10	8.18, 3.04, 2.88, 2.87	0.81

* The size of the signals were not marked if they were normal or in equal intensity; otherwise the weaker one would be indicated by (s).

** Solids deposited when more than one equivalent of DMF was added but dissolved as DMF reached seven molar equivalents.

rate with substituted tetracoordinate species. The ^{29}Si chemical shift of 19.5 ppm, 51.5 ppm away of Me_2SiI_2 to low field, suggested that the double substituted rather than the mono-substituted adducts were more likely to be the main complex in the equilibria, considering the strong shielding effect of iodine and the $\delta^{29}\text{Si}$ value being about -3 ppm for $[\text{Me}_2\text{Si}(\text{HMPA}^+)_2]$. The fact that ^{13}C of the methyl and ^1H of DMF were greatly deshielded meant DMF was coordinated. The very much broadened but not much shifted ^{13}C and ^1H signals of the Me_2Si moieties implied that Me_2SiI_2 was the dominant species in the equilibrium. That is understandable if the double substituted complex was the major substituted species in the equilibrium.

Further addition of DMF in to the mixture produced solids. These solids, isolated and found by elemental analysis to have a formula of $\text{Me}_2\text{SiI}_2 \cdot 2\text{DMF}$, redissolved when DMF reached seven equivalents relative to the silane. A slightly broadened ^{29}Si signal was observed at a higher field. The increase of ^{29}Si shielding demonstrated that there existed pentacoordinate species in equilibrium with DMF. The ^{13}C and ^1H spectra agreed with such a deduction. Therefore the interaction of Me_2SiI_2 with DMF can be expressed by Equation 2.10.



Equation 2.10

$\text{Me}_2\text{SiI}_2 + \text{DMPU}$

Additions of DMPU to Me_2SiI_2 produced only one additional ^{29}Si resonance signal in the range of 8.45~9.00 ppm, with more than 40 ppm difference from the silane and

independent of molar ratio, even at a quite low temperature (see Table 2.6). These results can be interpreted that only double replacement took place immediately after the addition of DMPU into Me_2SiI_2 and no pentacoordinate species formed under these condition.

Table 2.6 NMR data of the mixtures of Me_2SiI_2 + DMPU in CD_3CN + CDCl_3 .

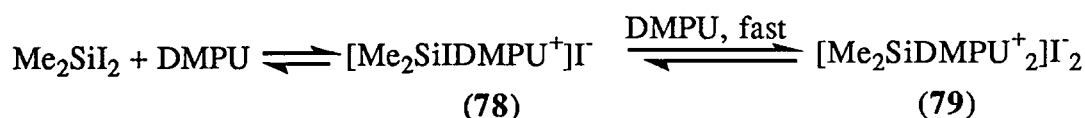
r	$\delta^{29}\text{Si}$ (ppm)	$\delta^{13}\text{C}$ (ppm)		$\delta^1\text{H}$ (ppm)	
		DMPU	Me_2Si	DMPU	Me_2Si
0.0	-33.96	(156.54, 47.85, 35.44, 22.17)	12.58	(3.26, 3.23, 2.89, 2.39, 1.98)	1.58
1.0*	-32.09	152.92(br),	13.16	3.91(br), 3.45,	1.76,
	-33.90	49.17(sbr), 40.27,	12.70	2.45(br)	1.58,
	8.45	20.16	2.47(br)		1.35
2.1	8.83	153.32, 48.66, 39.35, 19.82	1.95	3.73(br), 3.27, 2.28	1.17
3.0	8.89	154.65, 48.37, 38.03, 20.57	2.07	3.68, 3.62, 3.56, 3.15, 2.20	1.20
4.0	9.00	155.22, 48.20, 37.28, 20.97	2.01	3.60, 3.54, 3.47, 3.08, 2.15(br)	1.22
**	8.50	155.05, 48.03, 37.23, 20.85	1.84	3.54(t), 3.09, 2.14(q, sbr)	1.21

* There were two liquid phases present with this run, the others were homogeneous; the size of the signals were nearly the same.

** At 223 K.

The chemical shifts of ^1H and ^{13}C followed the general pattern of silane-nucleophile interaction. The Me_2Si moieties showed increased shielding and the chemical shifts moved to high field as the equilibria went to the formation of complexes. For the DMPU moieties, the proton deshielded upon donating electron density to silicon. The carbon-13 resonances were in accord with the usual observations on complexed species^{51b}; the methyl groups, C_4 , C_6 were deshielded and C_2 , C_5 shielded upon formation of adducts. Changes in the ^{13}C and ^1H chemical shifts when DMPU was present in more than two equivalents were owing to fast exchange of free DMPU with the complexed DMPU.

With equimolar amounts of Me_2SiI_2 and DMPU in solution, resonance signals of ^{29}Si , ^{13}C and ^1H of both Me_2SiI_2 and $[\text{Me}_2\text{SiDMPU}^+_2]\text{I}^-_2$ were observed but complicated by the presence of two phases. Nonetheless the interaction of DMPU with Me_2SiI_2 was very similar with that of HMPA and can be expressed accordingly (Equation 2.11).



Equation 2.11

Conductivity studies of $\text{Me}_2\text{SiI}_2 + r \text{ Nu}$

Some of the problems associated with conductivity measurements are illustrated by Figure 2.11. It was established by NMR that both NMI and DMF form pentacoordinate complexes with Me_2SiI_2 at high molar ratios of nucleophile to silane. On the other hand HMPA and DMPU do not cause the coordination at silicon to exceed four, even at high nucleophile to silane ratios. However, the conductivity titrations do not demonstrate this difference clearly. There are several reasons for this. The first is that for tetracoordination the conductivity increases in the expected

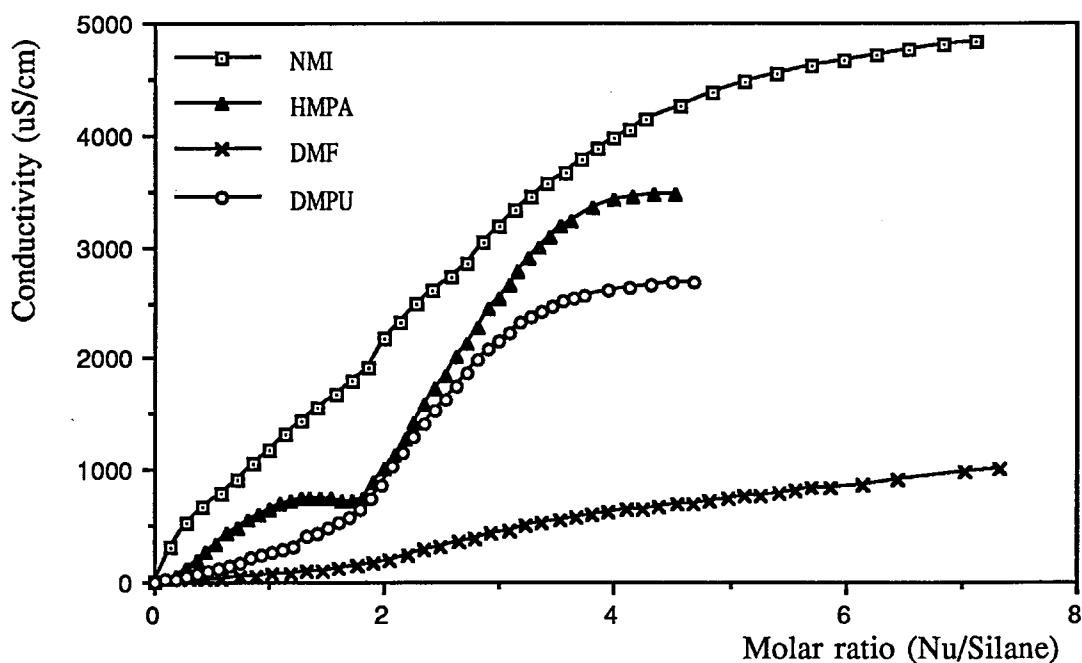


Figure 2.11 Conductivity titrations of Me_2SiI_2 with nucleophiles in CHCl_3 .

* 1 ml CH_3CN was necessary to dissolve the solids at ratio two with the NMI titration curve. The concentrations were 0.029 mmol./ml except with HMPA (0.021 mmol./ml).

way up to two molar equivalents of nucleophile. Subsequently, the addition of more nucleophile changes the solvent dielectric constant so the conductivity increases as tight ion pairing decreases. Without the NMR evidence it is almost impossible to differentiate this behaviour from that observed with pentacoordination. The effect is particularly marked in CHCl_3 . The only clue is that we observed that $\text{Me}_2\text{SiNu}^{+}_2$ and $\text{Me}_2\text{Si}^-\text{Nu}^{+}_3$ have almost identical conductivity. Therefore there is not usually any inflexion in the conductivity when pentacoordination follows tetracoordination. When the solvent dielectric constant or polarity changes but the coordination does not, there is often an inflexion at 2:1 Nu/Silane. That is clearly observed for HMPA/ Me_2SiI_2 but not so distinctly for DMPU.

2.2.4 The interaction of $\text{Me}_2\text{SiOTf}_2$ with nucleophiles

The triflate group is supposed to have a similar leaving and reacting abilities to iodide in silanes $\text{R}_3\text{SiX}^{51b}$. The interactions of $\text{Me}_2\text{SiOTf}_2$ with nucleophiles were found to

be equally exothermic to those of Me_2SiI_2 but the deposition of solid adducts took hours or even days in most cases.

$\text{Me}_2\text{SiOTf}_2 + \text{NMI}$

The ^{29}Si NMR spectra of the titration of $\text{Me}_2\text{SiOTf}_2$ against NMI showed the formation of pentacoordinate adducts (see Figure 2.12). The chemical shifts started

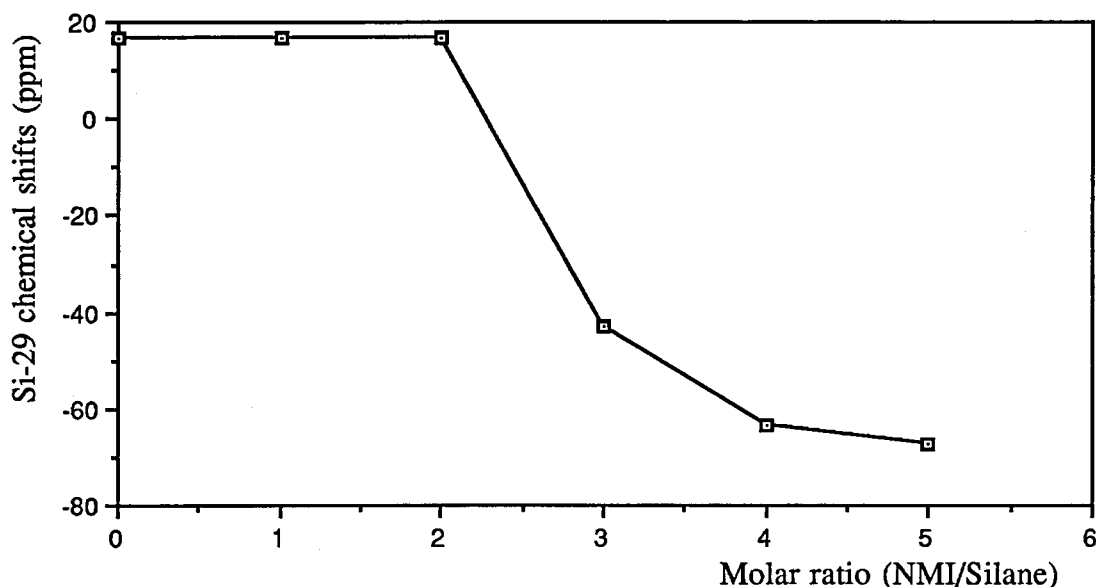


Figure 2.12 ^{29}Si titration of $\text{Me}_2\text{SiOTf}_2$ with NMI in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

* $c = 0.6 \text{ mmol./ml.}$

to move to high field after two molar equivalents of NMI were added and reached -68.4 ppm with five equivalents NMI. A $\delta^{29}\text{Si}$ value of -70.4 ppm was observed when neat NMI was used as solvent. At lower temperature (225K) with four equivalents NMI, a ^{29}Si resonance appeared at -74.0 ppm . All these ^{29}Si high field shifts demonstrated the existence of pentacoordinate species in the equilibrium. Solid adducts separated from the interaction have been proved by elemental analysis and ^1H NMR integrations to have the formula of $\text{Me}_2\text{SiOTf}_2 \cdot 3 \text{ NMI}$.

The ^{29}Si chemical shifts of the mixtures at molar ratios below two remained little changed from that of $\text{Me}_2\text{SiOTf}_2$, with an average of 16.6 ppm. This value was

concentration independent as well, though the chemical shift values of ^1H of the Me_2Si moiety changed from 1.13 to 1.31 ppm when the concentration of $[\text{Me}_2\text{SiNMI}^+_2]\text{OTf}^-_2$ increased from 0.21 to 1.53 mmol./ml and the proton signals of NMI were all deshielded. In contrast, $\delta^{29}\text{Si}$ values of $\text{Me}_2\text{SiOTf}_2$ with three equivalents of NMI were strongly dependent on the concentrations and shifted to high field with the increased concentration as the equilibrium favoured the formation of pentacoordinate adducts (see Figure 2.13). The unchanged ^{29}Si chemical shifts

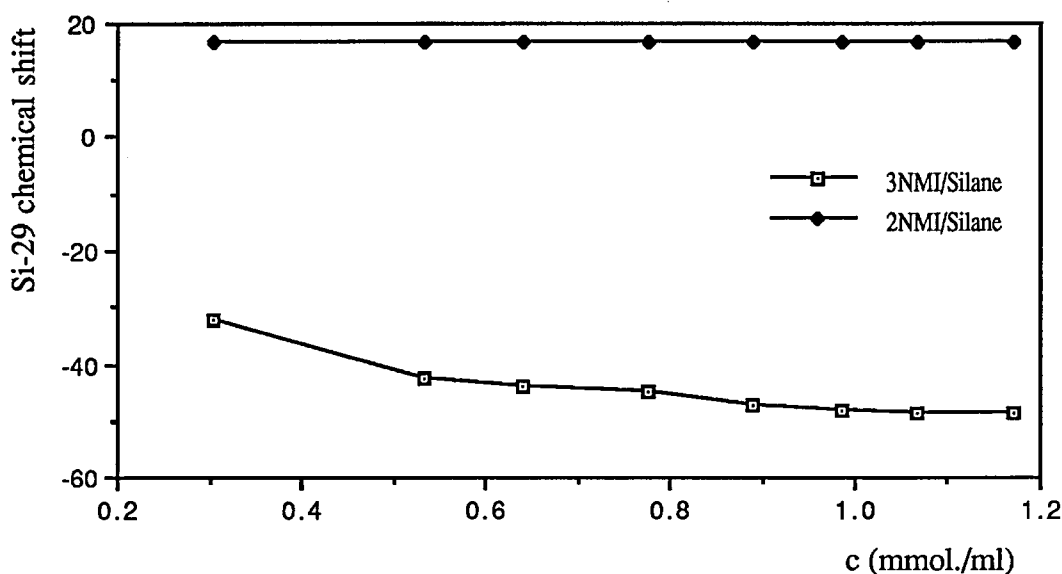


Figure 2.13 $\delta^{29}\text{Si}$ concentration dependence of $\text{Me}_2\text{SiOTf}_2 + r \text{ NMI}$ in CD_3CN .

below two equivalents of NMI were not because there was no chemical reaction but because the effect of OTf^- and NMI^+ on the chemical shift of silicon is the same in this case. Considering the sharp drop of $\delta^{29}\text{Si}$ values after two equivalents NMI in the titration curve, the formation of pentacoordinate adducts followed immediately after substitution of the two triflate groups.

$\text{Me}_2\text{SiOTf}_2 + \text{HMPA}$

The process of sequential substitution of the triflate groups of $\text{Me}_2\text{SiOTf}_2$ was more clearly demonstrated with HMPA by the ^{29}Si NMR spectra. The displacement of OTf^-

by HMPA caused the ^{29}Si resonance signal to split due to ^{31}P coupling under a slow exchange on the NMR time scale between HMPA and OTf, as shown in Table 2.7.

Table 2.7 NMR data of the mixtures of $\text{Me}_2\text{SiOTf}_2$ + r HMPA in CD_3CN + CDCl_3 .

	r	Temp.(K)	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{si-p}}$ (Hz)	$\delta^{31}\text{P}$ (ppm)
1	0.00	300	14.70		
2	0.54	300	14.81; 6.58, 6.09	8.8	
3	1.08	300	6.69, 6.25	7.8	26.89
		313	7.35(br)		
		323	Null		
4	1.50	300	6.97, 6.58; -2.69, -2.96, -3.24	6.8; 4.9, 4.9	
5	1.99	300	-2.69, -2.96, -3.24	4.9, 4.9	26.55,
		328	-2.69, -2.96, -3.24	4.9, 4.9	26.75
		333	-2.52, -2.91(sbr), -3.24	6.9, 5.9	
6	2.43	300	-3.10		
7	3.00	228	-3.13		

All the ^{29}Si NMR characteristic chemical shifts of the HMPA/ $\text{Me}_2\text{SiOTf}_2$ mixtures were within the range of tetracoordinate silicon. The doublets resulted from mono-substitution of one triflate group with one equivalent HMPA and the triplets

Me₂SiOTf₂ + DMF (or DMPU)

Similar titrations of Me₂SiOTf₂ with DMPU and DMF against ²⁹Si chemical shifts were carried out as illustrated in Figure 2.14. The ²⁹Si NMR chemical shifts of the

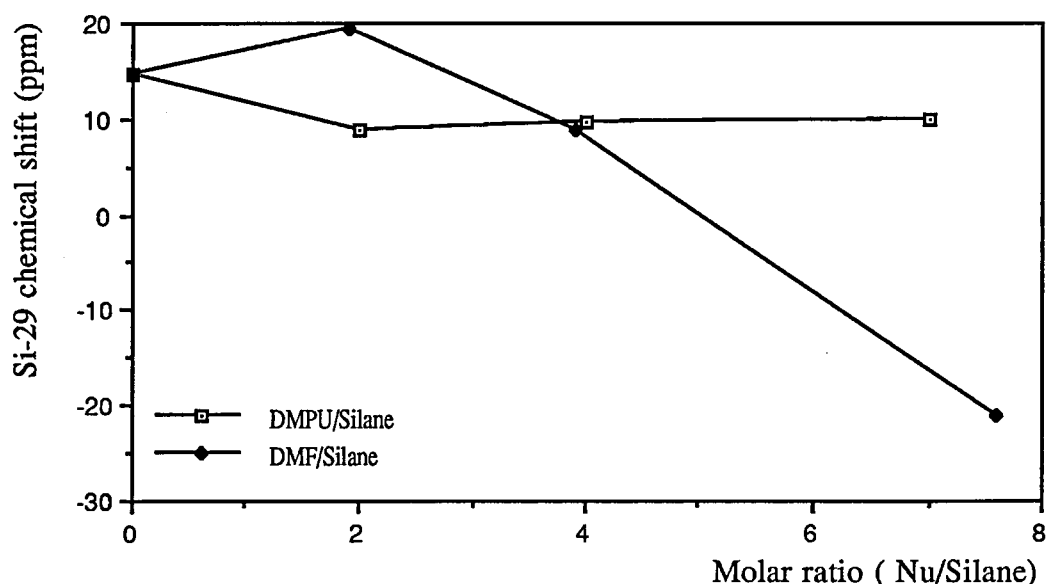


Figure 2.14 ²⁹Si NMR titrations of Me₂SiOTf₂ with nucleophiles in CD₃CN + CDCl₃

* c = 0.8 mmol./ml for DMF; c = 1.0 mmol./ml for DMPU.

mixtures of DMPU with Me₂SiOTf₂ remained around 10 ppm after an initial 7 ppm shift to high field even with increase the concentration of DMPU or at lower temperature (10.4 ppm at 228 K with seven equivalents of DMPU). The δ²⁹Si values suggested that the reaction was a simple substitution without any significant formation of pentacoordinate species.

By contrast, the ²⁹Si resonances were greatly shifted to high field on addition of DMF to Me₂SiOTf₂ with a ²⁹Si chemical shift of -21.2 ppm at 7.6 equivalents of DMF after an initial slightly deshielding at 1.85 equivalent DMF (19.3 ppm), which arose from substitution processes, and probably from doubly substituted complex formed as there was a small signal remaining at 14.9 ppm. Variable temperature studies (see Figure 2.15) indicated the equilibrium moved further towards formation of pentacoordinate

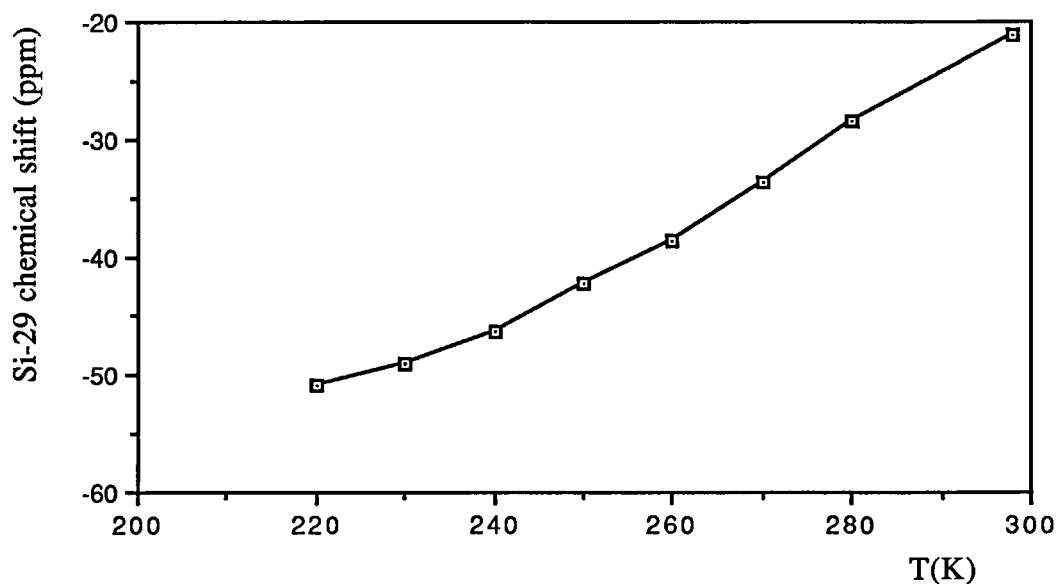
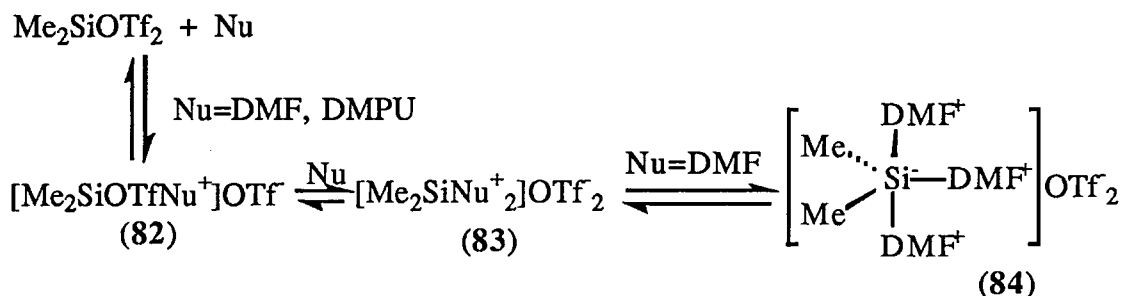


Figure 2.15 Variable temperature ^{29}Si study of $\text{Me}_2\text{SiOTf}_2 + 4 \text{ DMF}$

$c = 0.8 \text{ mmol./ml}$ in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

adducts as the temperature was lowered. $\delta^{29}\text{Si}$ values of -21.2 ppm at 298 K shifted to -51.0 ppm at 220 K with the most broadened signal between 250 and 260 K .

Therefore, although both DMPU and DMF are weak nucleophiles and have similar substitution pathways with $\text{Me}_2\text{SiOTf}_2$, their final complexes with $\text{Me}_2\text{SiOTf}_2$ are different. DMPU only forms tetracoordinate adducts while DMF can produce pentacoordination, as expressed in Scheme 2.2.



Scheme 2.2 Interactions of $\text{Me}_2\text{SiOTf}_2$ with DMF and DMPU.

Me₂SiOTf₂ + DMAP

Solid adducts were very readily deposited during the reaction of Me₂SiOTf₂ with DMAP. The $\delta^{29}\text{Si}$ values of 25.95 and 18.48 ppm were obtained respectively for molar ratios of DMAP to Me₂SiOTf₂ of three and five ($c = 0.08$ mmol./ml in CD₃CN + CDCl₃). A null signal was observed either with further increase of the molar ratio of DMAP to the silane or lowering the temperature (to 230 K) of the sample. The solids that separated have a formula of Me₂SiOTf₂·2DMAP. Therefore a double substitution reaction took place definitely in the mixture of Me₂SiOTf₂ with DMAP, but the formation of pentacoordinate species is less certain.

Conductivity studies of Me₂SiOTf₂ + Nu

Conductivity studies of the interaction of Me₂SiOTf₂ with nucleophiles in CH₃CN clearly demonstrated the formation of ionic species due to substitutions.

During titrations of Me₂SiOTf₂ with each of NMI, DMF, HMPA and DMPU the conductivities of the solutions increased steadily until they reached the maximal magnitudes (see Figure 2.16).

A point of inflexion for the HMPA titration curve was clearly marked at molar ratio (nucleophile to silane) of two. Extrapolation of the linear sections of the other curves would produce points of intersection all around molar ratio two as well. These points suggested that all these nucleophiles reacted with Me₂SiOTf₂ by way of reversible double substitutions except HMPA, which had a much larger equilibrium constant and was essentially irreversible. These results agreed with those deduced from the NMR spectra of the interacting mixtures.

The same conclusions could be reached by doing the conductivity titrations another way around, *eg.* titrating the individual nucleophiles with Me₂SiOTf₂, see Figure 2.17. The titration curves of NMI, DMF, HMPA, DMPU and DMAP all had a point of inflexion around molar ratio (silane to nucleophile) 0.5, *eg.* where silane:Nu = 1:2,

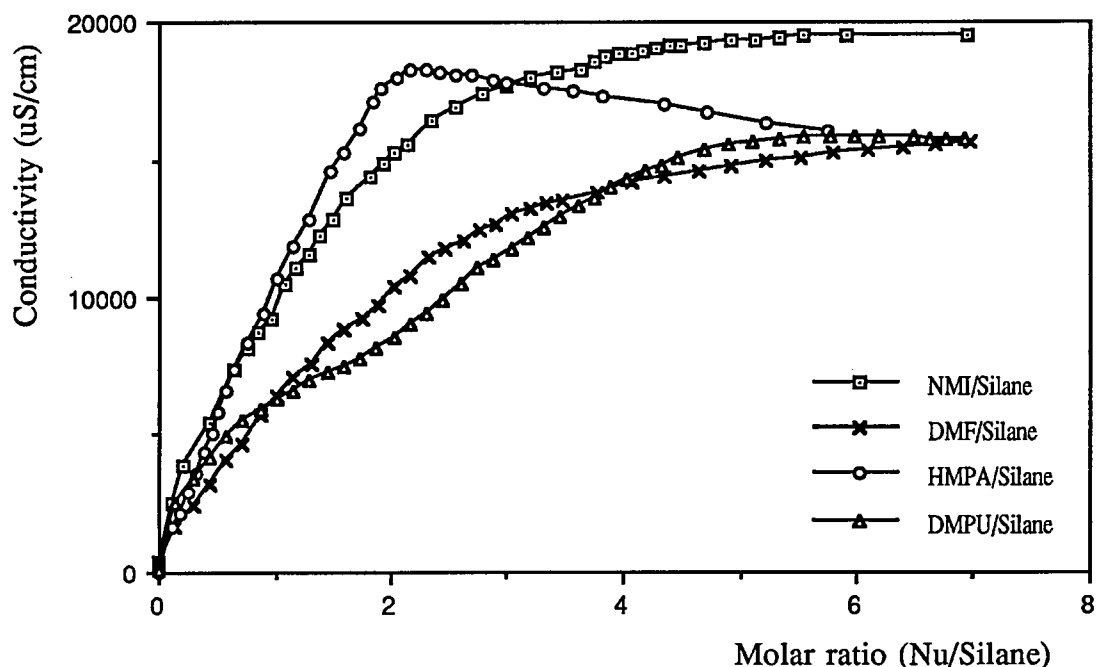


Figure 2.16 Conductivity titrations of $\text{Me}_2\text{SiOTf}_2$ with nucleophiles in CH_3CN .

* The concentrations of the silane were 0.21, 0.16, 0.14 and 0.25 mmol./ml for NMI, DMF, HMPA and DMPU respectively.

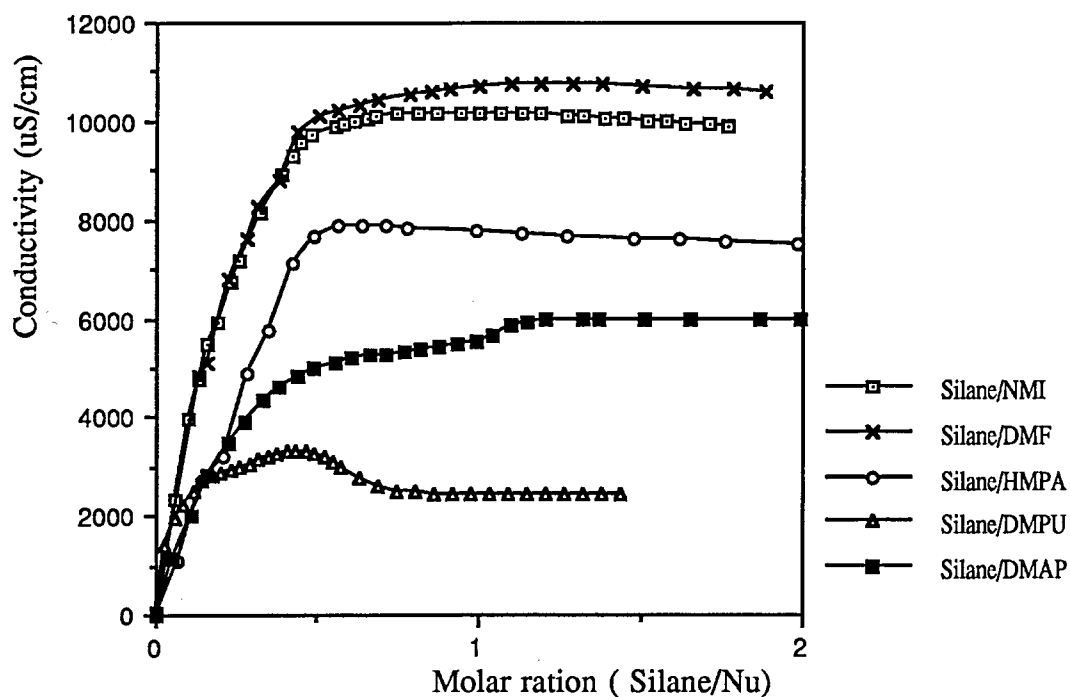


Figure 2.17 Conductivity titrations of nucleophiles with $\text{Me}_2\text{SiOTf}_2$ in CH_3CN .

* The concentrations were 0.21, 0.22, 0.10, 0.14 and 0.26 mmol./ml for NMI, DMF, HMPA, DMPU and DMAP respectively; 40% of the solvent were CHCl_3 in the DMPU and DMAP systems.

though the existence of CHCl_3 in the DMPU and DMAP systems affected the shape of their curves and the conductivity was lower in these solvent mixtures. The HMPA titration curve once again exhibited a sharper change, indicating a larger equilibrium constant than those of other interactions. Therefore the observations of the equilibria of $\text{Me}_2\text{SiOTf}_2$ with nucleophiles by conductivity studies were consistent with those by NMR, though tetra- and penta-coordinate silicon had similar conducting properties.

2.2.5 Cooperative reactions of $\text{Me}_2\text{SiOTf}_2$ with nucleophiles

The interaction of HMPA with $\text{Me}_2\text{SiOTf}_2$ showed a progressive substitution of the triflate groups with the nucleophile and the mono-substituted adducts were more stable towards further nucleophilic substitution than their parent silane. However, the progress of substitutions of the triflate groups with other nucleophiles examined were not so directly observed by ^{29}Si NMR for lack of such coupling. Consequently it was considered useful to examine the coordination reactions in the presence of two nucleophiles.

Cooperative reactions

The addition of two nucleophiles with equal molar quantity into $\text{Me}_2\text{SiOTf}_2$ solution resulted in an interesting equilibrium, in which the substituted species were detected by NMR, see Table 2.8 (DMST: $\text{Me}_2\text{SiOTf}_2$; NMR run in $\text{CD}_3\text{CN} + \text{CDCl}_3$, $c = 0.1$ mmol./ml). The astonishing stability of the substituted complexes clearly demonstrated that nucleophiles such as NMI, DMAP, DMF and DMPU would also displace the triflate groups of $\text{Me}_2\text{SiOTf}_2$ progressively when they were mixed with it as the NMR properties of the mixtures in Table 2.8 were not affected by the sequence of the nucleophiles being injected. In addition, the positions of the resonance of ^{29}Si reflected the contributions to the values of ^{29}Si chemical shift of individual nucleophiles upon substitution.

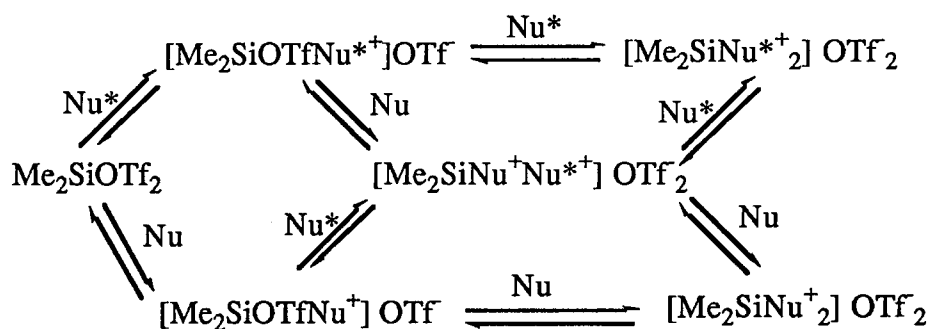
Table 2.8 NMR data of the mixtures of DMST with two equivalents of nucleophiles.

	1	2	3	4	5	6
	DMST* + r HMPA	DMST + HMPA + NMI	DMST + HMPA + DMAP	DMST + NMI + DMAP	DMST + HMPA + DMF	DMST + HMPA + DMPU
$\delta^{29}\text{Si}$ (ppm)	r=1: 6.75 (d, 7.9Hz) r=2: -2.85 (t, 4.9Hz)	16.35 6.80(d, 7.9Hz) -2.90(t, 4.9Hz)	26.28 12.34(d, 8.8Hz) -2.91(t, 4.9Hz)	26.22(s) 21.39(sbr) 16.44	7.95(d, 7.8Hz) -2.91 (s, sbr)	-2.91(t, 4.9Hz)
$\delta^{29}\text{Si}$ at 220K		15.96 6.36(d, 7.9Hz) -3.13(t, 4.9Hz)			7.68(d, 7.8Hz) -3.13(s, t, 4.9Hz)	8.50(s) 2.74(d, 6.8Hz) -3.18(t, 4.9Hz)
$\delta^{31}\text{P}$ (ppm)	r=1: 26.89 r=2: 26.55	26.92 26.62	26.79 26.37		26.32 26.55	26.79 26.52
$\delta^1\text{H}$ (ppm, Me ₂ Si)	r=1: 0.82 r=2: 0.77	1.04 0.76	1.04(sbr) 0.78(s)	1.29(br)	0.84(sbr)	0.81(sbr)
$\delta^1\text{H}$ (ppm, HMPA)	r=1: 2.85, 2.73 r=2: 2.86, 2.74	2.86, 2.74 2.77, 2.66	2.87, 2.75 2.78, 2.66		2.84, 2.72(sbr)	2.86, 2.74(sbr)
$\delta^1\text{H}$ (ppm, 3rd Nu)		9.02(sbr), 7.80, 7.56, 3.98(sbr)	7.9~8.45, 6.8~7.1, 3.30, 3.26	8.92, 8.10, 7.56, 6.95, 3.96, 3.27 (all br)	8.44(sbr), 3.45, 3.26	3.54, 3.12, 2.11(sbr)

In the interaction of $\text{Me}_2\text{SiOTf}_2$ with HMPA and strong nucleophiles such as NMI or DMAP, see Entry 2 and 3 in Table 2.8, a triplet at -2.9 ppm corresponding $[\text{Me}_2\text{Si}(\text{HMPA}^+)_2] \text{OTf}^-_2$ (81) was observed in both cases. Doublets at 6.8 and 12.3 ppm matching assorted doubly substituted adducts $[\text{Me}_2\text{Si}(\text{NMI}^+)(\text{HMPA}^+)] \text{OTf}^-_2$ and $[\text{Me}_2\text{Si}(\text{DMAP}^+)(\text{HMPA}^+)] \text{OTf}^-_2$ respectively were recorded. Therefore the $\delta^{29}\text{Si}$ values of 16.4 and 26.2 ppm were the chemical shifts of $[\text{Me}_2\text{Si}(\text{NMI}^+)_2] \text{OTf}^-_2$ (see also Figure 2.13) and $[\text{Me}_2\text{Si}(\text{DMAP}^+)_2] \text{OTf}^-_2$. ^1H and ^{31}P NMR studies verified such conclusions. Comparing the $\delta^{29}\text{Si}$ values of the cooperative substitution of NMI and DMAP with $\text{Me}_2\text{SiOTf}_2$ (Entry 4) with those in Entry 2 and 3, the ^{29}Si chemical shifts of doubly substituted adducts of NMI and DMAP were also at 16.4 and 26.2 ppm with another value of 21.4 ppm between them, corresponding to the mixed doubly substituted complex $[\text{Me}_2\text{Si}(\text{NMI}^+)(\text{DMAP}^+)] \text{OTf}^-_2$.

Weak nucleophiles such as DMF and DMPU were able to cooperate with the strongest nucleophile HMPA to displace the triflate groups of $\text{Me}_2\text{SiOTf}_2$ as well, see Entry 5 and 6 in Table 2.8. In both cases, apart from a large doublet, a small triplet was also observed on the ^{29}Si NMR spectra at low temperature. For DMPU, a tiny singlet was present too. Similar conclusions could be drawn following the same arguments, though there existed exchanges among the substituted species at room temperature. From the ^{29}Si resonance, the triplets at -3.1 ppm resulted from the doubly substituted adducts by HMPA. The doublets at 7.7 and 2.7 ppm were the signals of assorted substituted species, $[\text{Me}_2\text{Si}(\text{HMPA}^+)(\text{DMF}^+)] \text{OTf}^-_2$ and $[\text{Me}_2\text{Si}(\text{HMPA}^+)(\text{DMPU}^+)] \text{OTf}^-_2$ respectively. The singlet at 8.5 ppm corresponded the chemical shift of the doubly substituted complexes by DMPU, eg. $[\text{Me}_2\text{Si}(\text{DMPU}^+)_2] \text{OTf}^-_2$. ^1H and ^{31}P NMR data supported the assignment.

The sequence of the additions of the nucleophiles had practically made no difference of the chemical shifts and the shapes of the NMR signals of the mixtures. Therefore the interactions of two separate nucleophiles with $\text{Me}_2\text{SiOTf}_2$ could be expressed by the following scheme (Scheme 2.3):



Scheme 2.3 Nucleophilic substitution equilibria of $\text{Me}_2\text{SiOTf}_2$.

The observation that nucleophiles DMF and DMPU cooperated with HMPA to substitute the triflate groups to form quite stable substituted species indicated that $\text{Me}_2\text{SiOTf}_2$ and its mono-substituted adducts were labile and active enough to undergo substitution interactions with nucleophiles, no matter whether they were named “weak” or not. The equilibria of $\text{Me}_2\text{SiOTf}_2$ with nucleophiles were more dependent on the triflate as a good leaving group than on the nucleophilicity of the nucleophile. The $\delta^{29}\text{Si}$ values of the substituted complexes had no clear dependence on the nucleophilicities of the combined nucleophiles. The silicon-29 chemical shifts of the complexes were distributed irregularly along the combined Beta (Taft) values of the nucleophiles (see Figure 2.18). This may arise from the familiar U-shape $\delta^{29}\text{Si}$ values with substitution^{136d}.

However, it is noticeable that the values of the ^{29}Si chemical shifts of the complexes with two different nucleophiles were the mean of those complexes of doubly substituted adducts with a single nucleophile. From Table 2.8, every one displacement of HMPA by NMI or DMAP or DMPU would produce low field shifts of about 10, 14, 6 ppm respectively and vice versa. Similarly for the replacement of NMI by DMAP, a 5 ppm low field shift is always observed.

Applying this rule would allow a number of ^{29}Si chemical shifts of substituted complexes to be evaluated, which gave assistance to the interpretation of reaction mechanisms. For example, though the $\delta^{29}\text{Si}$ value of $[\text{Me}_2\text{Si}(\text{DMF}^+)_2]\text{OTf}_2^-$ was not

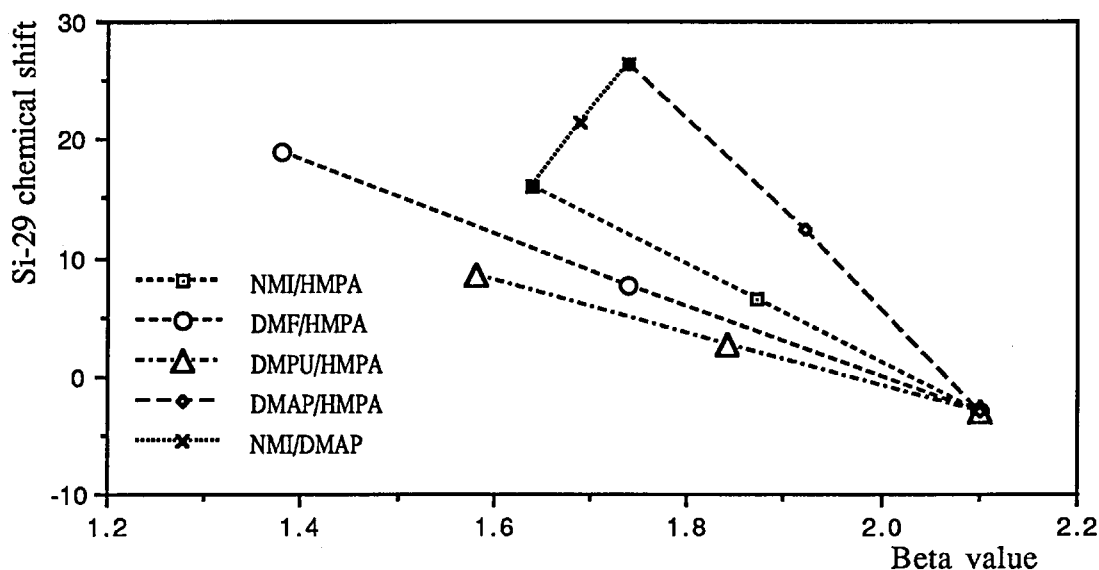


Figure 2.18 Relationship of $\delta^{29}\text{Si}$ values with the combined Beta values of the nucleophiles of the complexes $[\text{Me}_2\text{SiNu}^+_{(2-n)}\text{Nu}^{*+}_n] \text{OTf}^-_2$.

$n = 0, 1, 2$; $c = 0.1 \text{ mmol./ml}$ in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

obtained in the competitive reaction with HMPA, it could be estimated to be about 19 ppm as replacing HMPA by DMF was about 11 ppm down field shift (see Entry 5 of Table 2.8). This estimated value successfully matched the value of 19.3 ppm observed during titration study of $\text{Me}_2\text{SiOTf}_2$ with DMF (Figure 2.14) and the value of 19.5 ppm from the mixture of $\text{Me}_2\text{SiI}_2 + 0.9 \text{ DMF}$ (Table 2.5). For the interaction of DMAP with $\text{Me}_2\text{SiOTf}_2$, the observation of $\delta^{29}\text{Si}$ values of 26.0 and 18.5 ppm at the corresponding molar ratio (DMAP / DMST) three and five separately could be understood, without doubt, as an equilibrium between the doubly substituted adducts and the pentacoordinate complexes because the only explanation of the high field shift (18.5 ppm) on adding more DMAP to the already double substituted adducts (26.0 ppm) was the formation of pentacoordinated species.

Competitive reactions

Increases in the quantities of the nucleophiles in the cooperative interactions with $\text{Me}_2\text{SiOTf}_2$ resulted in an extra equilibrium between the doubly substituted adducts and the hypercoordinate species, see Table 2.9. The chemical shifts of silicon-29 of

Table 2.9 $\delta^{29}\text{Si}$ values of the mixtures of DMST with two nucleophiles.

	DMST + 2 DMAP	DMST + 2 HMPA	DMST + 2 HMPA	DMST + 2 HMPA	DMST + 2 HMPA
2nd Nu	+ 2NMI	+ 2 NMI	+ 2DMAP	+ 2 DMF	+ 2DMPU
$\delta^{29}\text{Si}$ (ppm)	-32.3(sbr)	-6.3(s, sh), -8.6(sbr)	1.3	-1.7(s), -8.3	-2.2(s), -8.6
at 220 K	-54.6(br)	-6.7(s)	-4.0(br)	-2.4(s),-8.5	-2.6(s),-8.8
2nd Nu		+ 4NMI	+ 4DMAP	+ 4DMF	+ 4DMPU
$\delta^{29}\text{Si}$ (ppm)		-5.6(s), -25.0(sbr)	-0.7	-1.9(s), -8.4	-2.1(s), -8.5

* c = 0.1 mmol/ml, refereed to the silane, in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

the mixture of two equivalents of NMI and DMAP with one equivalent of $\text{Me}_2\text{SiOTf}_2$ appeared at high field (-54.6 ppm at 220 K), which suggested the predominant species in the equilibrium to be five coordination at silicon. The up-field shift indicated NMI and DMAP were not competing with each other for substitution any more but combined together to build a pentacoordinate complex, which both of them had the capacity to form independently.

The ability of HMPA to produce pentacoordinate adducts is very much in doubt for Me_2Si derivatives with HMPA only, probably because of its large steric size rather than its nucleophilicity. However the ^{29}Si resonance signals of the mixtures of DMST and HMPA, *eg.* $[\text{Me}_2\text{Si}(\text{HMPA}^+)_2]$, and strong nucleophiles such as NMI or DMAP showed that HMPA contributed to the formation of pentacoordinate complexes as the chemical shifts matching $[\text{Me}_2\text{Si}(\text{HMPA}^+)_2]$ slightly moved to high field or disappeared. For NMI, the $\delta^{29}\text{Si}$ signal at about -6.3 ppm, nearly independent of

temperature, could correspond to a small amount of pentacoordinate complex in equilibrium with the tetracoordinate complex $[\text{Me}_2\text{Si}(\text{HMPA}^+)_2]$ while the resonance at -8.6 ppm, which shifted to -25.0 ppm with four equivalents of NMI and broadened at 220 K, might come from a pentacoordinate adduct in an equilibrium in which one of the components of the adduct was $[\text{Me}_2\text{Si}(\text{HMPA}^+)(\text{NMI}^+)]$. In this way, the small size of the signal at about -6 ppm could be explained. In the case of DMAP, there was only one signal observed. The chemical shifts values with further addition of DMAP or lowering the temperature were within a very narrow band close to tetracoordinate silicon.

The interactions of $\text{Me}_2\text{SiOTf}_2$ with quantities of HMPA and weak nucleophiles such as DMF or DMPU were difficult to interpret as the two pairs of signals at about -2 and -8.6 ppm were not affected neither by low temperature nor by increase the quantities of the weak nucleophiles.

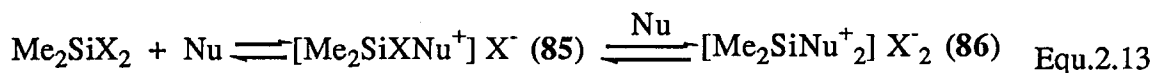
Therefore the formation of pentacoordinate complexes of $\text{Me}_2\text{SiOTf}_2$ in the presence of two nucleophiles with large quantities depended on both electronic and steric properties of the nucleophile. Two different nucleophiles could cooperate to enhance or hinder the expansion of coordination at silicon.

2.2.6 Summary

Silicon-29 NMR, together with proton, carbon-13 and phosphorus-31 NMR, proved to be invaluable for studying the substitution and coordination chemistry of dimethylsilyl species in solution.

The interactions of dimethyldifunctional silanes Me_2SiX_2 with nucleophiles were predominantly substitution when the nucleophiles were in low concentration. Pentacoordinated complexes formed with less space demanding nucleophiles at high concentration.

The substitution equilibria of Me_2SiX_2 with nucleophiles, as shown in Equation 2.13,



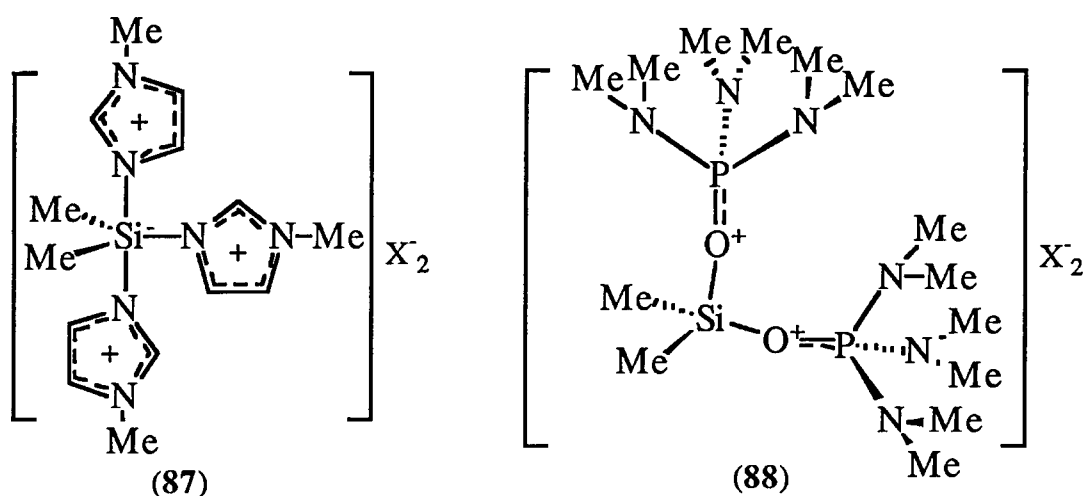
depended on both the leaving ability of the leaving groups (X) and the nucleophilicity of the attacking nucleophiles (Nu). The better the leaving groups, the more reactive the mono-substituted species and the easier the substitution. The leaving ability of the X groups in Me_2SiX_2 was in the order: $\text{Cl} \ll \text{Br} < \text{OTf} < \text{I}$, which was in agreement with the general observations^{51b, 95}. Stronger nucleophiles HMPA NMI and DMAP pushed the equilibria more to the right than weaker nucleophiles DMPU and DMF did.

The highest coordination number observed at silicon for the dimethylsilyl species reacting with nucleophiles was five. No evidence for the formation of hexacoordinate silicon was found at all. This probably resulted from the steric hindrance upon expansion of coordination at silicon. The ability for nucleophiles to construct pentacoordinated silicon with Me_2SiX_2 did not depend on the leaving groups of the silanes, nor on the Beta (Taft) values of the nucleophiles, nor on the kind of donor atoms (N or O), but on the possible steric effects from the nucleophiles. Take NMI and HMPA for an example, see Table 2.10. The similarity of the NMR properties of

Table 2.10 NMR data for the mixtures of Me_2SiX_2 with NMI or HMPA in solution.

X	Me_2SiX_2		$\text{Me}_2\text{SiX}_2 + r \text{ NMI}$		$\text{Me}_2\text{SiX}_2 + r \text{ HMPA}$	
	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)
Cl	34.2	0.82	-74.4	1.24	2.1	0.89
Br	22.0	1.12	-75.8	1.32	-2.9	0.94
I	-33.2	1.59	-75.3	1.32	-3.2	0.89
OTf	16.8	0.88	-74.0	1.23	-3.1	0.82

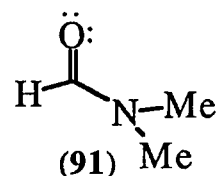
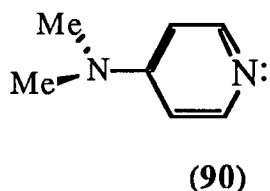
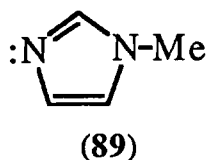
the mixtures with each nucleophile reacting Me_2SiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OTf}$) suggested the structures of the ultimate adducts were the same for each individual nucleophile and were independent of the leaving groups. NMI, with a smaller Beta (Taft) value of 0.80, produced pentacoordinate complexes (87) while HMPA, with a larger Beta (Taft) value of 1.05, only resulted in doubly substituted tetracoordinate adducts (88), see Scheme 2.4.



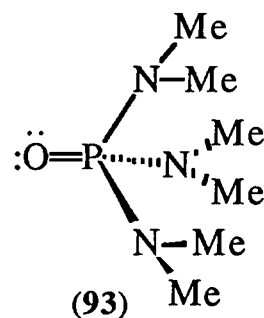
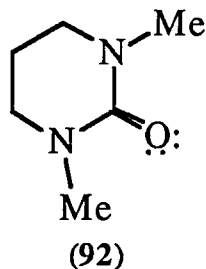
Scheme 2.4 Illustration of the structures of dimethylsilyl adducts.

Therefore the nucleophiles can be divided into two categories according to their capability to increase the coordination number at silicon. The first group contains those will produce pentacoordinate adducts with Me_2SiX_2 and have a smaller possible steric hindrance. NMI (89), DMAP (90) and DMF (91), see Scheme 2.5, belongs to this group (Nu^{I}). All of these nucleophiles had shown the ability to produce pentacoordinate silicon with dimethylsilyl species, though their individual nucleophilicity might well affect the equilibrium constant. The other group (Nu^{II}) includes those nucleophiles, represented by DMPU (92) and HMPA (93), which only formed tetracoordinate adducts with Me_2SiX_2 and were more space demanding. The nucleophilicities of the nucleophiles could affect the equilibrium constants for the substitution equilibria but did not alter the character of the ultimate adducts which have coordination number one less than those of the first group. However, the

The first group Nu^I:



The second group Nu^{II}:



Scheme 2.5 Illustration of the structures of nucleophiles.

cooperation of the nucleophiles from group one and group two might lead to the increase of coordination at silicon if the steric effects were in favour. The kind of donor atoms of the nucleophile did not make much difference to the coordination number at silicon as oxygen donors were presented in both categories.

The reactivity of the dimethylsilyl species relied heavily on the functional groups. Though the strongest exothermic phenomena were usually observed with the addition of the first equivalent of nucleophile to the silane, the silane-nucleophile adducts were not necessarily more reactive than their parent compounds. The equilibria between Me_2SiX_2 and nucleophiles were temperature dependent and low temperature favoured the formation of silane-nucleophile bonds. Chlorosilanes were particularly inactive compared with those of bromide, iodide and triflate.

Solvation and stabilization of the adducts were increasingly important in the solution study of the interaction of Me_2SiX_2 with nucleophiles as electrical charges accumulated progressively with the reaction progress. Every substitution of X with a neutral nucleophile forms a pair of separate ions. Doubly substituted adduct, such as **88**, had two positive charges around silicon. Association of a third nucleophile forming

a pentacoordinate structure, such as **87**, would add another internal ion pair. With such a high number of cations surrounding silicon, the solvation by organic solvents, even by polar ones, would be limited. The stabilization of the cations largely came from the cleaved counter anions. Therefore, on the one hand, the chemical shifts of the adducts might slightly alter with the changing of the counter anions (X^-). On the other hand, solid complexes in the nucleophilic reactions with multi-functional silanes were more ready to deposit, even co-deposited with solvents and chemically unbonded nucleophiles in extreme cases. With small-sized, hard counter anions such as Cl^- and Br^- , solids might precipitated at an early stage, *eg.* having a formula of $Me_2SiX_2 \cdot 2 Nu$. With large-sized soft counter anions, including I^- and OTf^- , precipitation only occurred when complexes of formulae $Me_2SiX_2 \cdot 3 Nu$ (*eg.* $Me_2SiX_2 \cdot 3 NMI$) were formed in the solution.

The solvation and stabilization of the ionic species were of special importance in the conductivity study of the interaction of Me_2SiX_2 with nucleophiles in solution. With weak or non-polar solvents like $CHCl_3$, the stabilization of the positive charges on the silyl moiety relied mainly on the counter anions and internal dispersion. Therefore the magnitude of the conductivity of the mixtures was lower than expected as the ion pairs were quite tight and surrounded by non-conducting media. The formation of a pentacoordinate complex only changed the mass of the species. In the presence of polar solvents such as CH_3CN , or even free nucleophiles, the cleaved ion pairs could be separated by solvation and the solvents themselves also had an enhanced polarity induced by the ions. Consequently the conductivity of the solution will be greater. Nonetheless the conductivity titrations in particular solvents successfully described the substitution processes.

On the whole, the interactions of dimethyldifunctional silanes with nucleophiles proceeded by an initial substitution without expansion of coordination at silicon. Pentacoordinate complexes, if sterically allowed, followed the doubly substituted adducts as more nucleophiles were added. Only the interaction of Me_2SiCl_2 with NMI might be an exception, in which case the second substitution of chlorine might take

place simultaneously with the formation of pentacoordinated species.

2.3 The interactions of PhMeSiCl_2 and Ph_2SiCl_2 with nucleophiles

The replacement of the methyl group by phenyl in the trialkylsilane $\text{R}_3\text{R}_2\text{R}_3\text{SiX}$ was found to increase the reactivity of the silane and the possibility of coordination expansion at silicon^{51b, 53}. The alcoholysis of Ph_2SiCl_2 was reported to proceed by way of mono-substituted tetracoordinated ionic intermediate². As has been stated above, for the interaction of Me_2SiX_2 with nucleophiles, the reactivity was attributed to the leaving groups and the expansion of coordination at silicon determined by the possible steric hindrance. Within this sub-section the effects of the methyl group being replaced by phenyl group towards coordination at silicon in the difunctional silane will be studied.

2.3.1 The interactions of PhMeSiCl_2 with nucleophiles

The interactions of MePhSiCl_2 , like those of Me_2SiCl_2 , were observed to be exothermic with strong nucleophiles such as NMI, DMAP and HMPA but this could hardly be detected with weak nucleophiles such as DMF and DMPU. The adducts were more readily soluble in organic solvents than those of Me_2SiCl_2 .

$\text{MePhSiCl}_2 + \text{NMI}$ (or HMPA)

Titration of MePhSiCl_2 with NMI or HMPA led ^{29}Si resonances of the mixtures to shifting to high field, see Figure 2.19. Like the situation with Me_2SiCl_2 , NMI reacting with MePhSiCl_2 caused the ^{29}Si chemical shifts to move to the range of pentacoordinated silicon, with more than 70 ppm difference at a molar ratio of seven, while HMPA only resulted in about a 5 ppm high field shift and the silicon remained tetracoordinate. The ^{29}Si resonance signals were progressively broadened with diminishing intensity as the concentration of NMI increased and those with HMPA were just slightly broadened. These results indicated that there were pentacoordinate

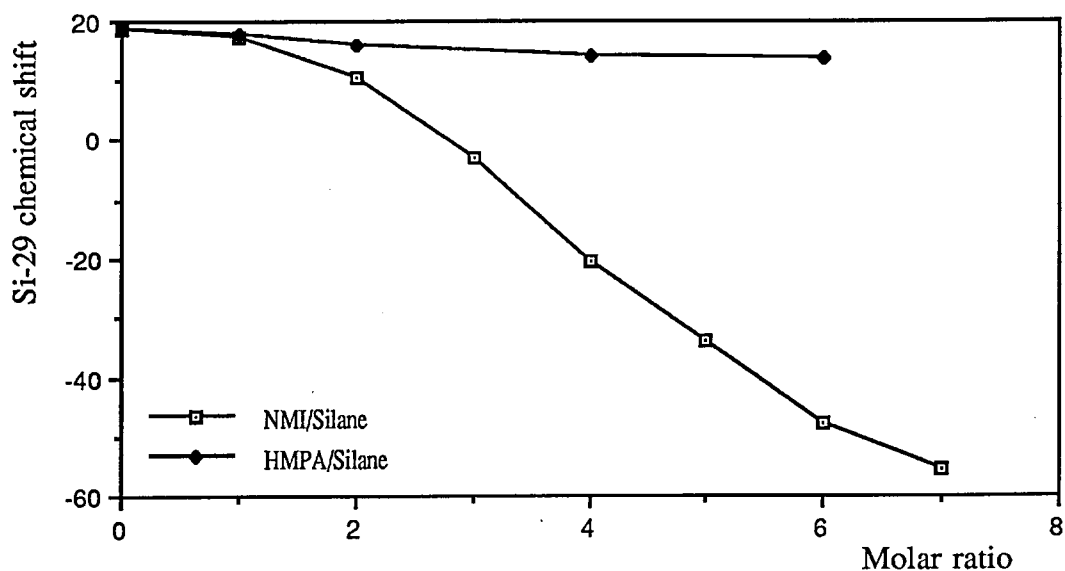


Figure 2.19 ^{29}Si NMR titrations of MePhSiCl_2 with nucleophiles in CDCl_3 .

* The concentrations referred to MePhSiCl_2 were 0.60 and 0.44 mmol./ml in the NMI and HMPA systems respectively.

silicon species with NMI and only tetracoordinate silicon species with HMPA in the equilibria.

However, the proton chemical shifts of the MePhSi moiety during the titration with NMI supplied little information about the formation of pentacoordinate silicon except for the methyl protons of the MePhSi moiety, which were increasingly deshielded with a maximum shift of 0.3 ppm, see Figure 2.20. The distances between the two sets multiplets of the phenyl group (measured by their highest peaks hereinafter) did not become larger, though the signals grew more and more broadened, as is usual for hypercoordinate silicon¹³⁶. This might be attributed to a fast exchange in which a tetracoordinated species is dominant. This was proved to be true by variable temperature NMR study of the mixture, see Table 2.11. The ^{29}Si chemical shifts shifted to higher field as the temperature of the sample was lowered down with the most broadened signal at 243 K. The protons were more deshielded as well, recorded at 223 K where the pentacoordinate silicon species became dominant in the equilibrium according to the ^{29}Si NMR signals. The significance of the observation of

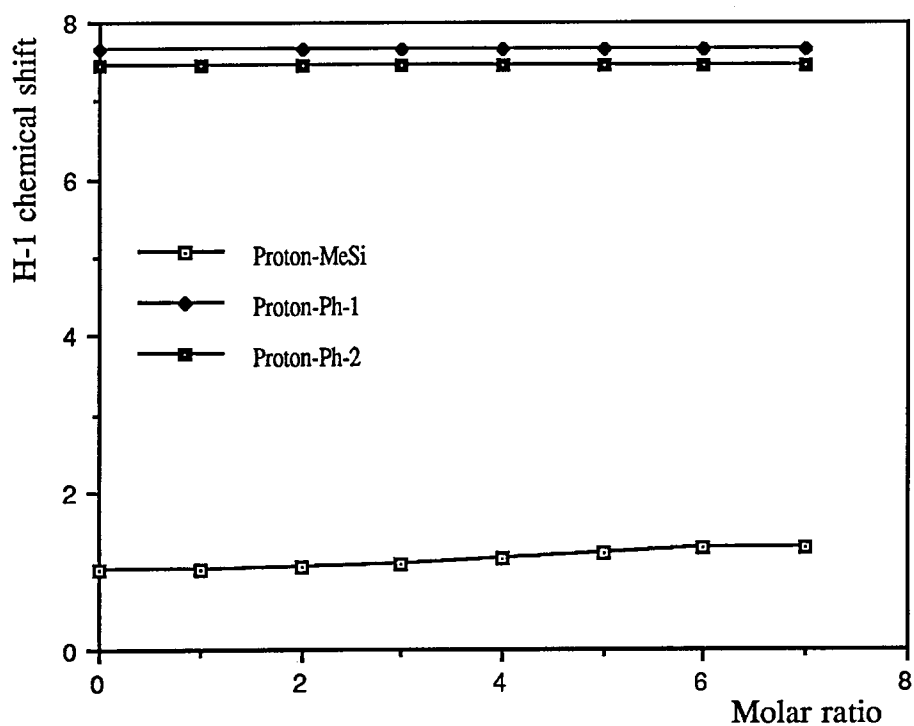


Figure 2.20 Proton NMR titration of MePhSiCl₂ with NMI.

* c = 0.44 mmol./ml referred to MePhSiCl₂ in CDCl₃.

Table 2.11 Variable temperature study of MePhSiCl₂ + 6 NMI.

Temperature (K)	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)		
		MeSi	PhSi	NMI
300	-43.12(br)	1.26(br)	7.65(br) 7.48(br)	7.83, 7.04, 6.98, 3.71(all sbr)
263	-75.00(br)			
243	-80.53(vbr)			
223	-82.40(br)	1.55(br)	7.75(br) 7.51(br)	8.17, 7.18, 6.97, 3.80(all sbr)

* c = 0.44 mmol./ml referred to MePhSiCl₂ in CDCl₃.

the proton chemical shifts was that they showed that the distance between the two sets of multiplets of the phenyl signals did increase as the coordination at silicon expanded or vice versa.

Conductivity studies of MePhSiCl₂ + NMI (or HMPA)

Conductivity studies of the interactions of MePhSiCl₂ with NMI and HMPA by titrations showed that the conductivity of the mixtures greatly increased at high nucleophile to silane molar ratios and verified the substitution reaction with production of ionic species, see Figure 2.21. However the conductivity readings at the

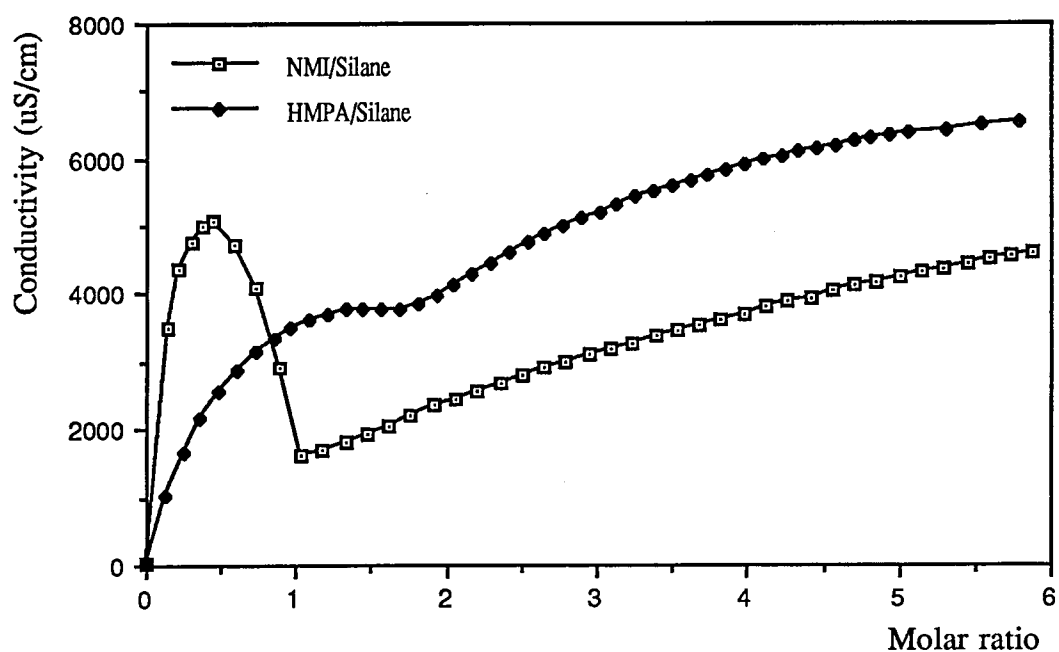
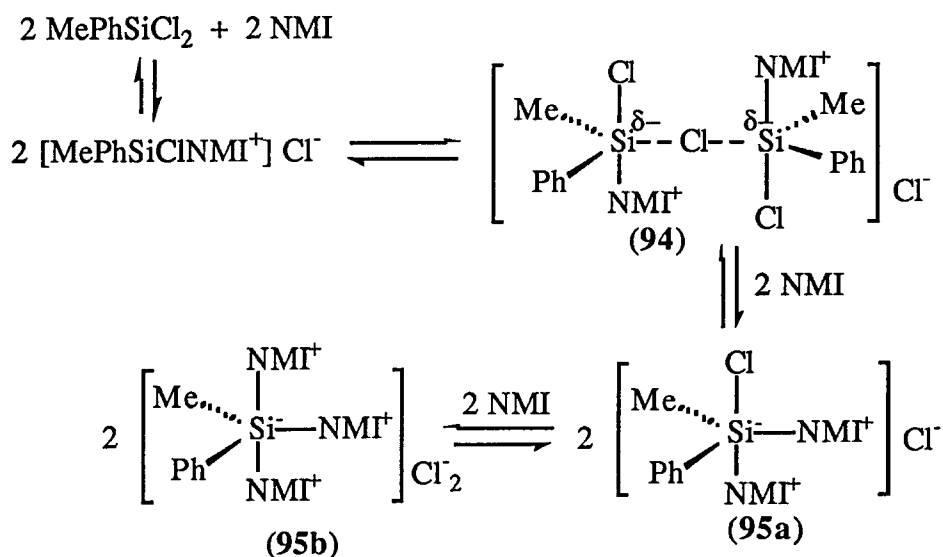


Figure 2.21 Conductivity titrations of MePhSiCl₂ with nucleophiles in CH₃CN.

* The concentrations were 0.33 and 0.19 mmol./ml referred to MePhSiCl₂ respectively with NMI and HMPA.

early stages of the titrations became complicated. Though the initial dramatic increases of conductivity of the mixtures might suggest a greater equilibrium constant for substitution reaction than those of Me₂SiCl₂, there was a sharp conductivity drop for NMI from molar ratio 0.5 to one and a delay for HMPA around 1.5 equivalents of

HMPA. In the latter case, it could be interpreted that the mono-substituted intermediate $[\text{MePhSiCl}(\text{HMPA}^+)] \text{Cl}^-$ was stable and the additional substitution was difficult. For NMI, it was probably because of the strong nucleophilicity of Cl^- , which engaged in an equilibrium with the mono-substituted adducts to form loose pentacoordinations with a chlorine bridged between them. The continued substitution of chlorine was most likely to take place within the pentacoordinate structures as the conductivity of the solution was increased smoothly with the continual addition of NMI and ^{29}Si chemical shifts moved quickly to high field. Therefore the substitution process of MePhSiCl_2 with NMI could be expressed by the following scheme (Scheme 2.6):



Scheme 2.6 Reaction pathways of MePhSiCl_2 with NMI.

$\text{MePhSiCl}_2 + \text{DMAP}$ (or DMF, DMPU)

The interactions of MePhSiCl_2 with other nucleophiles selected were comparable with those of Me_2SiCl_2 (see Table 2.1 and 2.12). The interaction of DMAP with MePhSiCl_2 showed clear signs of the formation of pentacoordinate silicon complexes, marked by the high field shift of the ^{29}Si resonance, which heavily depended on the temperature of reaction. However, there were hardly any significant chemical

Table 2.12 NMR data of the mixtures of MePhSiCl₂ with nucleophiles in CDCl₃.

	6DMAP (c=0.3)		6DMF (c=0.3)		6DMPU (c=0.6)		6HMPA (c=0.44)	
Temp.	300 K	228K	300 K	223 K	300 K	228K	300 K	223 K
$\delta^{29}\text{Si}$	15.84	-56.8 (vbr)	19.04	19.04	19.15	18.98	13.88	Null
$\delta^1\text{H}$ MeSi	1.08	1.71	1.02	1.04	1.04	1.05	1.06	1.31(br)
PhSi*	7.64 7.47	7.58(br)	7.68 7.50	7.68 7.47	7.67 7.51	7.71, 7.51	7.69 (sbr), 7.54 (sbr)	7.80(br), 7.62(br)
Nu	8.20~8.13, 6.47~6.40, 2.91	8.10(br), 6.59(br), 3.05	8.02, 2.95, 2.85	8.03, 2.96, 2.85	3.23(t), 2.88, 1.94(qu)	3.19, 2.89, 1.93	2.72, 2.61	2.73, 2.69

* The two sets of multiplets of the phenyl group(s) were represented by their highest signals in each case hereinafter unless specified.

interactions between weak nucleophiles, such as DMF and DMPU, and both silanes, Me₂SiCl₂ and MePhSiCl₂. The slightly changed chemical shifts in these mixtures could be attributed to solute-solvent interactions.

2.3.2 The interactions of Ph₂SiCl₂ with nucleophiles

Ph₂SiCl₂ + NMI

NMR titration studies of the interaction of Ph₂SiCl₂ with NMI showed that the ²⁹Si resonances shifted significantly to high field progressively with the addition of NMI and reached -62.2 ppm at a molar ratio (NMI/Ph₂SiCl₂) of seven, with the most broadened and weak signal at five equivalents of NMI, see the titration curve in

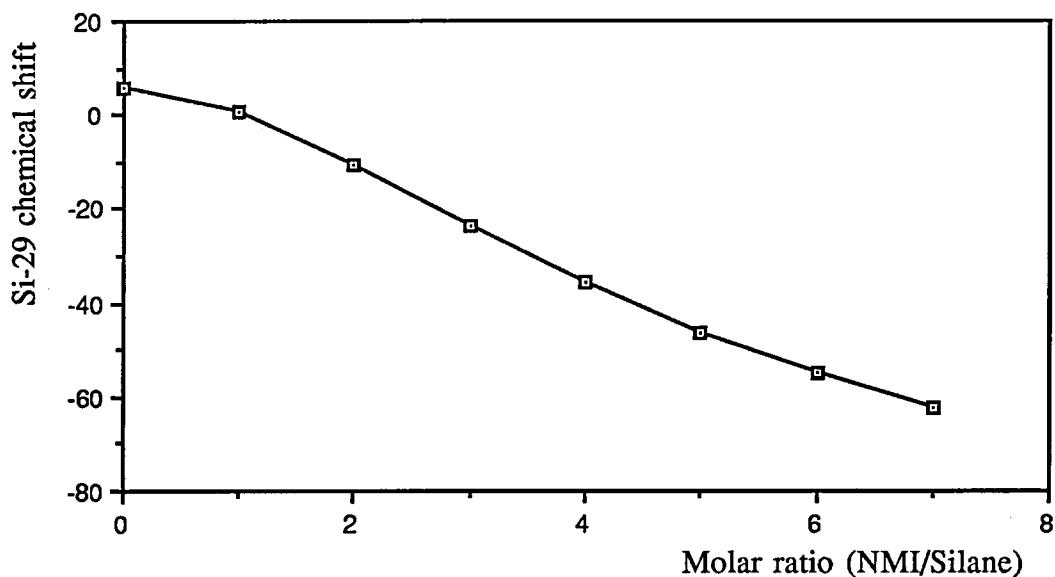


Figure 2.22 $\delta^{29}\text{Si}$ titration of Ph_2SiCl_2 with NMI in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

* $c = 0.45 \text{ mmol./ml}$ according to Ph_2SiCl_2 .

Figure 2.22. The 68 ppm high field shift from that of Ph_2SiCl_2 clearly indicated the existence of pentacoordinate silicon species in the equilibria. The proton NMR spectra had also supported the suggestion of the formation of five-coordinated silicon. The distances between the two sets of multiplets of the Ph_2Si moiety increased slowly after an initial decrease, where NMI was less than two equivalents, see Figure 2.23.

A combination of the NMR properties of the Ph_2Si moiety of the titration would suggest that the substitution of chlorine with NMI was the dominant interaction between NMI and Ph_2SiCl_2 when the concentration of NMI was low, *eg.* with low NMI to Ph_2SiCl_2 molar ratio. However, considering the rather strong nucleophilicity of Cl^- and the low equilibrium constants usually observed with chlorosilanes, it was perhaps unlikely that the formation of pentacoordinate silicon complexes was based on doubly substituted adducts. Therefore the last chlorine substituted was most likely by pentacoordinate silicon intermediate, as shown in Scheme 2.7, in which complex **96** was in equilibrium with complex **97** and the mono-substituted adduct. NMR signals at low temperature gave such indication as well. In the mixture of Ph_2SiCl_2 with six equivalents of NMI at 228 K, see Entry 1 of Table 2.13, there were two closely

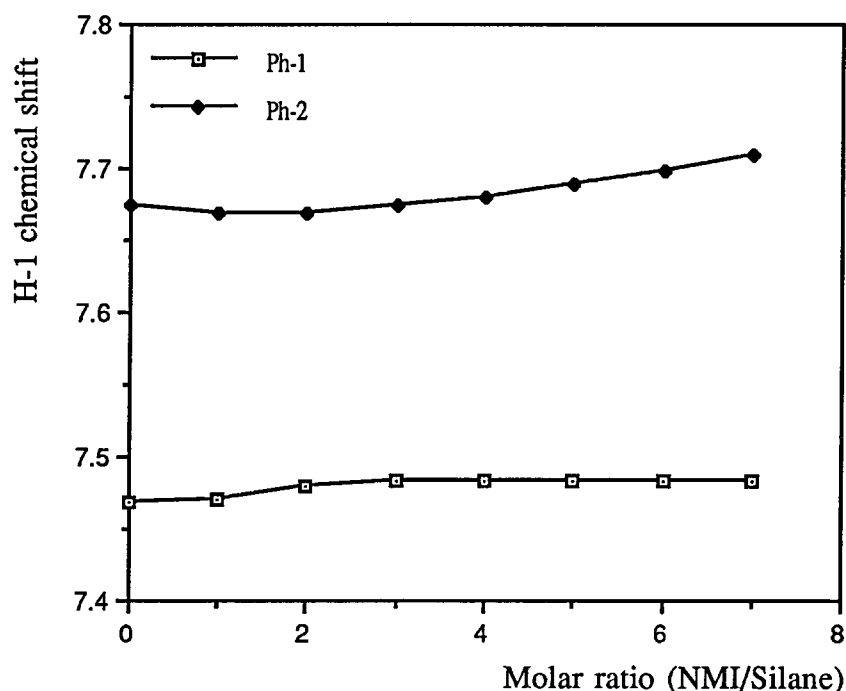
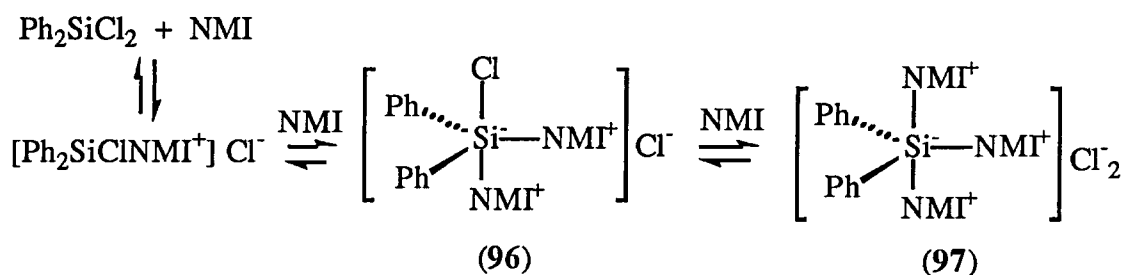


Figure 2.23 $\delta^1\text{H}$ titration of Ph_2SiCl_2 with NMI in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

* $c = 0.45 \text{ mmol./ml}$ according to Ph_2SiCl_2 .



Scheme 2.4 Reaction pathways of Ph_2SiCl_2 with NMI.

positioned slightly broadened ^{29}Si signals at higher field (-95.4 and -96.5 ppm) with nearly equal intensities. On the proton NMR spectrum, there were also two peaks with almost equal intensities for the methyl group of NMI, though the signals at low field were broadened and overlapped. These two sets of signals corresponded to the complexes **96** and **97** in equilibria with each other and with $[\text{Ph}_2\text{SiClNMI}^+] \text{Cl}^-$ and NMI at slow rates of interconversion at the temperature. The failure to observe such signal splits at room temperature was perhaps that the exchange rate among them was too fast.

Table 2.13 NMR data of the interactions of Ph₂SiCl₂ + r Nu in CDCl₃.

	r Nu	Temp. (K)	c*	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)	
					Ph ₂ Si	Nu
1	6NMI	300	0.57	-70.22(vbr)	7.72, 7.47	7.66, 7.03, 6.88, 3.63
		228		-95.35, -96.50 (both sbr)	7.77~ 6.78** 3.75, 3.53(all br)	
2	6DMAP	300	0.22	3.62	7.66, 7.47(br)	8.18, 6.45, 2.90(all br)
		223		-72.53(br)	7.91, 7.51(br)	6.48, 2.99(all br)
3	6DMF	300	0.46	6.09	7.69, 7.52	8.01, 2.92, 2.82
		220		-5.87	7.69, 7.53(br)	8.06, 2.95, 2.84(all sbr)
4	6HMPA	300	0.46	1.87	7.68, 7.57	2.68, 2.57
		220		-16.02(br)	7.71(vbr)	2.71, 2.60(sbr)
5	6DMPU	300	0.46	6.14	7.68, 7.52	3.20(t), 2.87, 1.91(qu)
		220		5.98	7.68, 7.53(sbr)	3.20(t), 2.88, 1.90(sbr)

* The concentrations were in mmol./ml referred to Ph₂SiCl₂.

** The signals were broadened and overlapped.

Ph₂SiCl₂ + DMAP (or HMPA, DMF and DMPU)

The interactions of Ph₂SiCl₂ with other strong nucleophiles such as DMAP and HMPA (Entry 2 and 4 of Table 2.13) showed that DMAP produced pentacoordinate silicon complexes while HMPA resulted in substituted tetracoordinated adducts in

equilibria at low temperature, marked mainly by the ^{29}Si high field shift from 6.03 ppm (Ph_2SiCl_2) to -72.5 and -16.02 ppm respectively. The proton NMR data also displayed such complexations in the equilibria. However, in contrast with those of Me_2SiCl_2 and MePhSiCl_2 , clearly exothermic interactions was observed for Ph_2SiCl_2 with weak nucleophiles such as DMF and DMPU, though the chemical shifts of silicon-29 of the mixtures were just shifted by 8.9 ppm to high field for DMF and hardly any movement was observed for DMPU, even at a rather low temperature of 220 K (see Entry 3 and 5 of Table 2.13). Nonetheless the high field shift for DMF with Ph_2SiCl_2 was large enough to attribute to chemical reactions between the weak nucleophile DMF and Ph_2SiCl_2 . Although it was not conclusive yet whether the process was substitution within tetracoordinate silicon, probably so, or association with expansion of coordination at silicon at fast equilibrium, the results were adequate enough to suggest that Ph_2SiCl_2 was the most reactive silane towards nucleophilic attack within the examined dichlorosilane $\text{R}^1\text{R}^2\text{SiCl}_2$ ($\text{R}^1, \text{R}^2 = \text{Me}, \text{Ph}$) series.

Conductivity studies

Conductivity studies with the titration of Ph_2SiCl_2 by NMI, HMPA and DMF also showed each interaction mixture had its own conducting character but agreed with its results observed with ^{29}Si and ^1H NMR studies. The correlations of their conductivities against the nucleophile/ Ph_2SiCl_2 molar ratios are illustrated in Figure 2.24. The shape of the NMI curve was more like that with Me_2SiCl_2 than the one with MePhSiCl_2 . The conductivity readings for the DMF titration were quite small which matched the weak interaction found by NMR study at room temperature. The shape of the HMPA curve was very much alike with the one with MePhSiCl_2 and could be explained in the same way.

2.3.3 Summary

The interactions of $\text{R}^1\text{R}^2\text{SiCl}_2$ ($\text{R}^1, \text{R}^2 = \text{Me}, \text{Ph}$) with nucleophiles were comparable both in their reactivity and coordination chemistry.

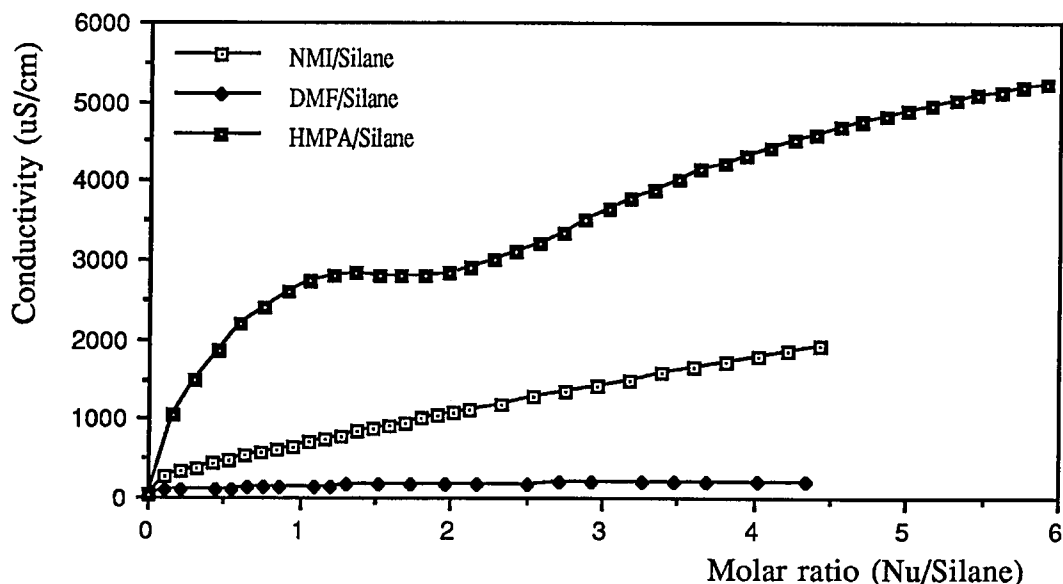


Figure 2.24 Conductivity titrations of Ph_2SiCl_2 with nucleophiles in CH_3CN .

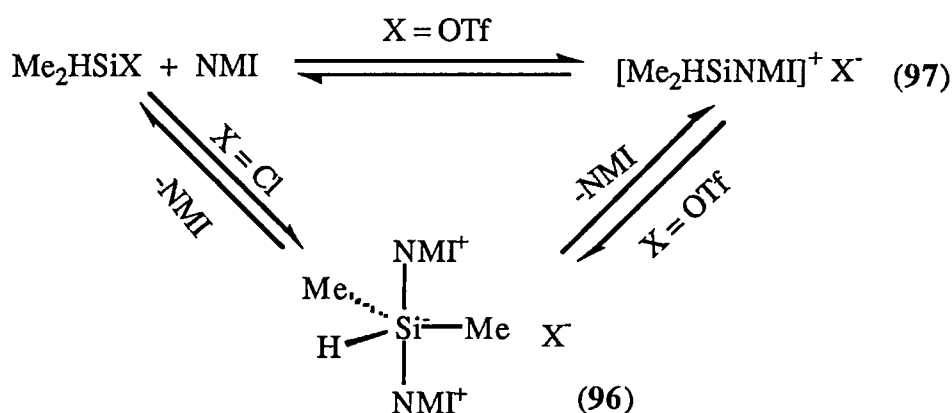
$c = 0.19, 0.24$ and 0.19 mmol./ml for the titration of NMI, DMF and HMPA respectively.

Every replacement of a methyl group with phenyl increases the reactivity of the silane towards nucleophilic interaction, probably because phenyl had a better ability to stabilize the charge formed in the reactions. The reactivity of the silanes could be expressed in the order of $\text{Ph}_2\text{SiCl}_2 > \text{MePhSiCl}_2 > \text{Me}_2\text{SiCl}_2$. The increased reactivity of phenyl difunctional silanes was in agreement with those observed with $\text{R}^1\text{R}^2\text{R}^3\text{SiX}$ ($\text{R}^1, \text{R}^2, \text{R}^3 = \text{Me, Ph}$)^{51, 100}.

Both tetra- and penta-coordinated silicon complexes were produced. No evidence was found for the existence of hexacoordinated silicon. At low nucleophile/silane molar ratio, tetracoordinated species were the dominant in the equilibrium, which agreed perfectly with Frye's results². At high Nu:silane molar ratio, pentacoordinate complexes could be formed with one or two chlorine atoms being replaced. However, the formation of pentacoordinate silicon adducts was limited to those nucleophiles with the least possible steric hindrance. No evidence was found to disagree with the divisions of nucleophiles in sub-section 2.2.6.

2.4 The interactions of RHSiX_2 ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{Cl, OTf}$) with nucleophiles

The interactions of mono-functional silanes R_3SiX ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{Halogen, OTf}$) with nucleophiles in solution were reported to be substitutions, forming only tetracoordinate adducts^{5, 6, 51, 52, 99, 100}. Although pentacoordinate silicon was proposed, there was no direct evidence found. However, the interactions of H-containing mono-functional silanes R_2HSiX ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{Cl, OTf}$) with NMI, DMAP and DMF were observed to produce pentacoordinate silicon complexes^{51, 52, 53, 102}. A reaction pathway was described, represented by Me_2HSiX and NMI, as shown in Scheme 2.8. That meant a replacement of an alkyl or aryl



Scheme 2.8 Reaction pathway for Me_2HSiX with NMI

group by hydrogen could increase the maximum available coordination number at silicon by one. Nonetheless the formation of pentacoordinate species like **96** with HMPA was not conclusive. For example, the mixture of $\text{Me}_2\text{HSiOTf} + 5$ HMPA resulted in null ^{29}Si NMR signal^{51b}. The claimed -59.5 ppm ^{29}Si chemical shift at 200 K for $\text{MePhHSiCl} + 3$ HMPA⁵³ was found to be the product of disproportionated silane. The true δ ^{29}Si value was -11.6 ppm by re-examination of the interaction at the same conditions.

The interactions of difunctional silanes R_2SiX_2 ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{Halogen, OTf}$) with

nucleophiles, as stated above, were similar to those of H-containing mono-functional silanes as far as coordination chemistry concerned. In this section, the interactions of H-containing difunctional silanes RHSiX_2 ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{Cl, OTf}$) with nucleophiles will be examined to see if those coordination differences at silicon from mono-functional silane were similar with difunctional silanes.

2.4.1 The interactions of RHSiCl_2 ($\text{R} = \text{Me, Ph}$) with nucleophiles

The silicon coordination chemistry in the interactions of acyclic silanes with the choice nucleophiles mentioned above were strongly influenced by the steric property around silicon. Therefore the interactions of RHSiCl_2 with nucleophiles in solution will be discussed according to the steric demand of the nucleophiles, not their nucleophilicities.

The nucleophiles, NMI, DMAP and DMF, which all favoured pentacoordination with R_2SiX_2 were firstly examined in the reaction with RHSiCl_2 . The interactions were all exothermic. The stronger nucleophiles, such as NMI and DMAP, were found to precipitate solid adducts readily in various solvents.

$\text{MeHSiCl}_2 + \text{NMI}$

An NMR study of the interaction of MeHSiCl_2 with NMI in solution indicated hexacoordinate silicon complexes were the most stable adducts on the NMR time scale. Chemical shifts in silicon-29 and proton NMR spectra of the mixtures at various NMI: MeHSiCl_2 ratio are shown in Table 2.14. The ^{29}Si resonances of the mixtures of MeHSiCl_2 with NMI were null signal until four equivalents of NMI was added. The new single sharp signal was more than 180 ppm higher field from that of MeHSiCl_2 . The $\delta^{29}\text{Si}$ value of -170 ppm was in the range of hexacoordinate silicon. Actually the appearance of this signal marked a change in the NMR properties of the mixtures. Any extra addition of NMI hardly affected the line shapes of either ^1H or ^{29}Si NMR of the MeHSi moiety, though the protons were deshielded and the coupling constant between ^{29}Si and ^1H increased progressively with the injection of NMI when

Table 2.14 NMR data of the interaction of MeHSiCl₂ + r NMI.

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}$ (ppm)		
			Si-H	Si-Me	NMI
0	11.44	281.6	5.59(q)	0.91(d)	(7.37, 6.96, 6.85, 3.53)
1	Null	Null	5.65(q,sbr)	0.97(d,sbr)	8.98, 7.26, 7.20, 3.92(sbr)
2	Null	Null	5.75(sbr)	1.11(sbr)	9.08, 7.34, 7.22, 3.93(sbr)
3	Null	Null	5.82(sbr)	1.22(sbr)	9.08, 7.27, 7.20, 3.94(sbr)
4	-170.39(sh)	328.3	5.88(sbr)	1.34(sbr)	8.99, 7.29, 7.19, 3.93(sbr)
5	-170.48(sh)	326.8	5.88(sbr)	1.34(sbr)	8.72, 7.23, 7.14, , 3.88(sbr)
6.3	-170.56(sh)	326.8	5.88(sbr)	1.34(sbr)	8.46, 7.18, 7.10, 3.82(sbr)

c = 0.9 mmol./ml referred to MeHSiCl₂ in CD₃CN + CDCl₃.

$r \leq 4$. The proton resonances of NMI, having been kept strongly deshielded, also became less deshielded after the ²⁹Si signal at -170 ppm appeared. The latter case was due to fast exchange between the free and the associated groups of NMI. The slightly broadened proton signals of all the mixtures supported such exchange processes between nucleophiles including chlorine, though intramolecular pseudorotation might also attribute to the line shape because of the symmetries of the complexes. Therefore the interaction of MeHSiCl₂ with NMI was an equilibrium between many species resulting in hexacoordinate silicon species in the end.

PhHSiCl₂ + NMI

Similar NMR studies were carried out with the interaction between PhHSiCl₂ and NMI in various solvents and solids always came out of solution at an NMI/PhHSiCl₂

ratio of two or three. The NMR properties of the mixtures before precipitation were similar to those of MeHSiCl₂ with NMI. No signal was observed for ²⁹Si. The protons were deshielded to a similar degree except the phenyl protons, which were shielded by 0.05 to 0.17 ppm with the separation of the two sets of multiplets slightly decreased. This might indicate there were equilibria involving mainly tetracoordinate species in the early stage of the reaction.

Solid adducts of RHSiCl₂ + NMI

Solid adducts were isolated from the interactions of both MeHSiCl₂ and PhHSiCl₂ with NMI. Elemental analysis and NMR study of ¹H, ¹³C and ²⁹Si by re-dissolving the solids showed they were co-deposited with solvents, each had a formulae of MeHSiCl₂·3NMI·CH₃CN and PhHSiCl₂·3NMI·CDCl₃.

RHSiCl₂ + DMAP (or DMF)

NMR study of the interactions of RHSiCl₂ (R = Me, Ph) with DMAP and DMF at room temperature showed that hypercoordinate, most likely the hexacoordinate silicon adducts, in the equilibria were produced with DMAP but no significant reaction was observed with DMF at all. The changes of the chemical shifts of silicon-29 of the mixtures of RHSiCl₂ + r Nu are listed in Table 2.25.

In the interactions of DMAP with MeHSiCl₂ and PhHSiCl₂ at DMAP:silane ratio six, both had quite sharp signals at high field, -134.8 and -129.7 ppm with coupling constants of ²⁹Si-¹H 329.8 and 273.9 Hz respectively. It was conceivable that both MeHSiCl₂ and PhHSiCl₂ interacted with DMAP by the same pathway, though solids were more ready to deposit for the phenyl silane. The more than 145 and 127 ppm high field shifts from MeHSiCl₂ and PhHSiCl₂ respectively were also large enough to demonstrate the formation of hexacoordinate silicon complexes. The interactions of the weak nucleophile DMF at room temperature were insignificant as determined by ²⁹Si NMR, together with unchanged proton chemical shifts and ²⁹Si-¹H coupling constant.

Table 2.15 $\delta^{29}\text{Si}$ values of the mixtures of $\text{RHSiCl}_2 + r \text{ Nu}$ at room temperature.

Nu	R	c*	r=1	r=2	r=3	r=4	r=5	r=6
DMAP	Me	0.2	Null**	Null	Null	-80.04 (s,br)	-131.84	-134.79
	Ph	0.2	-	-	-	Solids***	-113.93	-129.66
DMF	Me	0.7	11.03	11.14	11.14	11.20	-	11.08
	Ph	0.6	-2.31	-	-2.31	-	-	-2.31

* The concentrations were referred to the silane where $r = 1$ in mmol.ml in CDCl_3 except $\text{PhHSiCl}_2 + \text{DMAP}$, which was in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

** There were also disproportionation reactions which will be discussed later.

*** The titrations for those of DMAP were mostly done by addition of the silane to the DMAP solution. There was precipitation if more PhHSiCl_2 was added here.

However, variable temperature studies by NMR spectroscopy of the mixtures of RHSiCl_2 with DMAP and DMF presented an interesting change. The chemical shifts of the mixtures at various temperature are shown in Table 2.16. The $\delta^{29}\text{Si}$ values of the solutions of RHSiCl_2 with six equivalents of DMAP only shifted to higher field by a few ppm, less than 2 ppm for MeHSiCl_2 from 300 K to 228 K and 12 ppm for PhHSiCl_2 from 300 K to 222 K ($J_{\text{Si-H}} = 304.86 \text{ Hz}$). Surprisingly, the ^{29}Si chemical shifts of the mixture of MeHSiCl_2 with six equivalents of DMF shifted from 10.5 ppm at 238 K to -164.2 ppm at 220 K with null signal at 228 K and sharp signals at both ends. Such a high field shift of silicon-29 was comparable with that of 4 NMI with MeHSiCl_2 and is interpreted as the formation of hexacoordinate silicon adducts in the equilibrium. However, the silicon-29 resonance of the mixture of PhHSiCl_2 with 6 DMF at 222 K resulted null signal. It seemed, in the case of RHSiCl_2 , that the phenyl replacing a methyl group had more labile silane-nucleophile complexes and was more

Table 2.16 Variable temperature studies of ^{29}Si NMR of $\text{RHSiCl}_2 + r \text{ Nu}$.

	6 DMAP		6 DMF	
	MeHSiCl ₂	PhHSiCl ₂	MeHSiCl ₂	PhHSiCl ₂
300	-134.79	-124.37	11.08	-2.85
288	-135.23		11.13	
278	-135.45		11.19	
268	-135.74		10.03	
258	-136.05		10.87	
248	-136.33		10.78	
238	-136.60		10.45(s)	
228	-136.22		nil	
222		-136.08	-164.22(sh)	Null

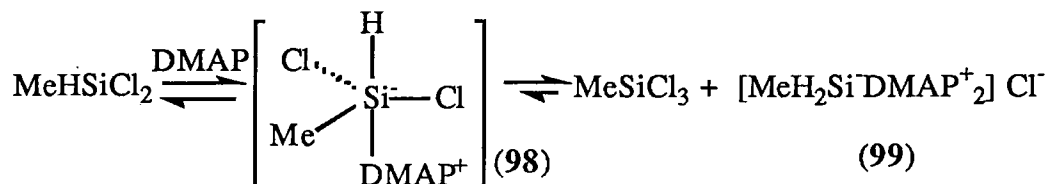
The concentrations of the silane were 0.2, 0.15, 0.7 and 0.65 from left to right in CDCl_3 except $\text{PhHSiCl}_2 + 6 \text{ DMAP}$, which was in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

ready to precipitate solid adducts.

Disproportionation reaction, $\text{MeHSiCl}_2 + \text{DMAP}$

It was noteworthy that the equimolar mixture of MeHSiCl_2 and DMAP produced a disproportionation of the silane. Although the mixture initially showed a null signal for the silicon-29 NMR, see Scheme 2.9, three new signals for ^{29}Si resonance were found, together with three sets of protons of the silane moieties a few days after the sample was made. Presumably MeHSiCl_2 was initially in a fast equilibrium with a

pentacoordinate intermediate **98**, which slowly disproportionated into MeSiCl₃ and dihydride complex **99**. The chemical shifts of ²⁹Si and ¹H observed with the mixture and listed under each assumed compound in Scheme 2.9 matched such a presumption



Instantly, c = 0.6 mmol./ml:

$\delta^{29}\text{Si}$	(11.44)	Null	(12.23)
$J_{\text{Si-H}}$	(281.6)	Null	(7.8)
$\delta^1\text{H}$	[5.59(q)	5.56(sbr)	(1.13)
(MeHSi)	0.91(d)]	0.84(d)	

Eight days later, 220 K:

$\delta^{29}\text{Si}$	Null	12.78	-78.83(sh)
$J_{\text{Si-H}}$	Null	8.8	270(t)
$\delta^1\text{H}$	5.49(br)	1.21	4.88
(MeHSi)	0.81(br)		0.26

c = 0.7 mmol./ml, two days after the sample has been made up:

$\delta^{29}\text{Si}$	-43.56(vbr)	12.94	-77.24(sh)
$J_{\text{Si-H}}$	288.11	8.8	538.13/2(t)
$\delta^1\text{H}$	5.54(sbr)	1.19	4.94
(MeHSi)	0.83(d)		0.32(t)

Scheme 2.9 The disproportionate reaction of MeHSiCl₂ with DMAP and its NMR properties.

* NMR were run in CD₃CN + CHCl₃. The data in brackets were only quoted for reference.

quite well. The pentacoordinate intermediate **98** was marked by a weak and much broadened ^{29}Si signal at about -43 ppm, which was more than 50 ppm high field than that of MeHSiCl_2 (11.44 ppm). The ^{29}Si - ^1H coupling constant and proton spectra indicated the Si-H bond remained. The chemical shifts assigned to MeSiCl_3 were reasonably close and overlapped the signals from MeSiCl_3 externally added into the mixture. The other disproportionation product **99** was identified positively. In the ^{29}Si NMR spectra, the chemical shift was at high field within the range of pentacoordinate silicon. There was a triplet indicating the silicon bonded with two hydrogen with coupling constants of 270 Hz approximately. As MeSiCl_3 hardly associated with DMAP and dihydrosilane was more reactive towards nucleophilic reaction^{51b}, DMAP was bound to react with the dihydrosilane. In the proton spectra, a triplet corresponding to a methyl group coupling with two hydrogen ($J_{\text{H-H}} = 2.7$ and 2.5 Hz) was observed at about 0.3 ppm though the multiplet for the protons of Si-H bond at 4.94 ppm was a little indistinct and only one coupling constant of 2.7 Hz was measurable.

However, the disproportionation reaction of RHSiCl_2 was observed only with MeHSiCl_2 and DMAP at 1:1 molar ratio. The enhanced reactivity of the Si-H bond possibly resulted from an apical position of the Si-H bond due to pseudorotation in the pentacoordinate complex. The hexacoordinate species seemed to have a more stable Si-H bond as no disproportionation reaction was found. A solid adduct that separated from MeHSiCl_2 with three equivalents of DMAP was analyzed by elemental analysis and solution NMR to have a formula of $\text{MeHSiCl}_2 \cdot 3 \text{ DMAP}$.

Conductivity studies, $\text{MeHSiCl}_2 + \text{NMI}$ (or DMAP or DMF)

Conductivity measurements showed that the additions of NMI and DMAP into MeHSiCl_2 or vice versa increased the conductivity of the mixtures but DMF had hardly any effect at room temperature, see Figure 2.25. The immediate large increases of conductivity of MeHSiCl_2 solution upon the addition of NMI indicated a substitution process, see **100** in scheme 2.10. The decreases of conductivity of the solution as

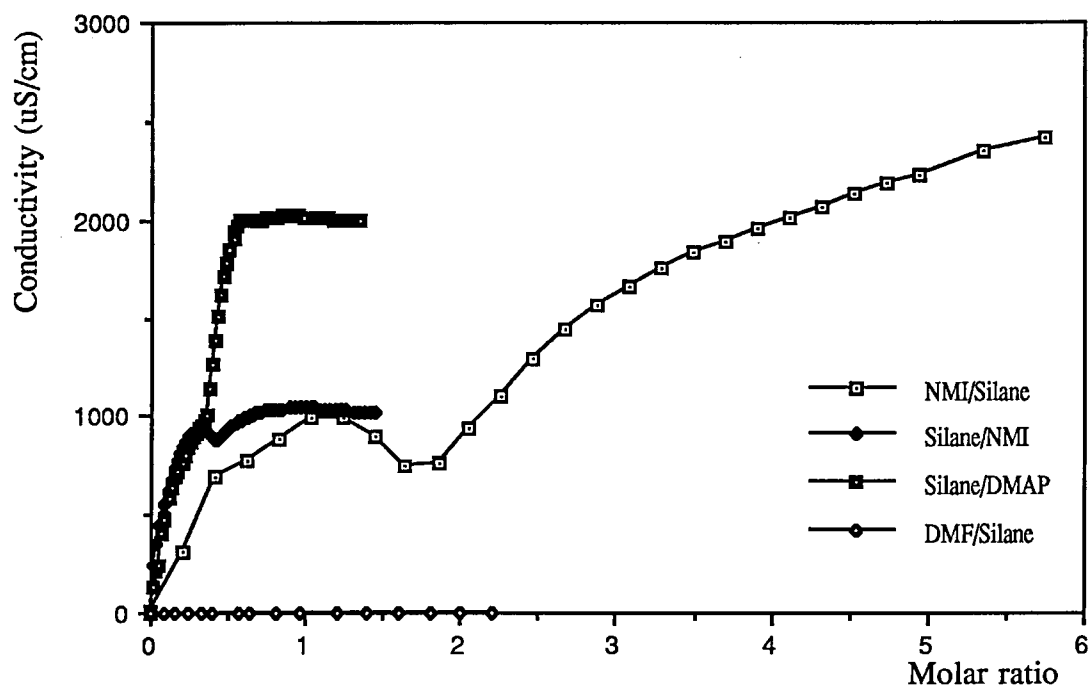
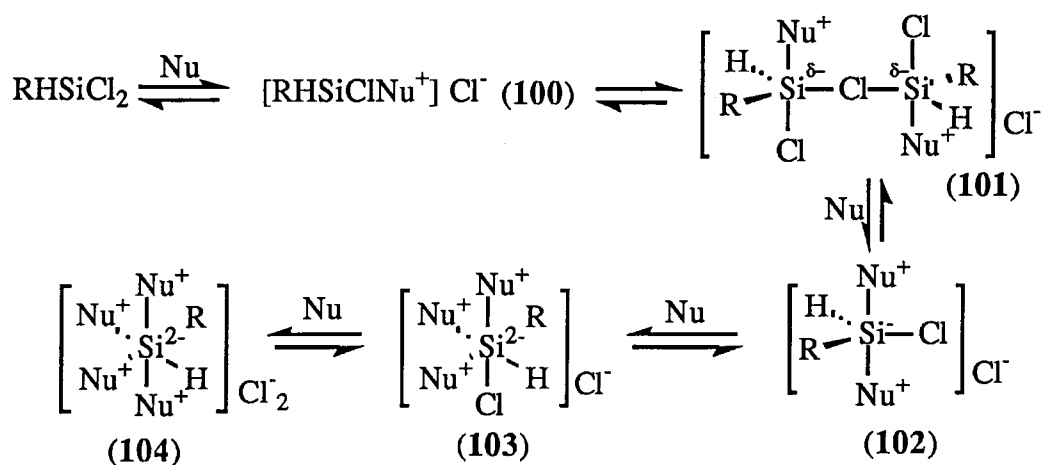


Figure 2.25 Conductivity titration studies of MeHSiCl₂ and nucleophiles.

The concentrations were 0.4 mmol./ml related to the titrate except the one titrating with NMI ($c = 0.25$); all were in CD₃CN + CDCl₃ except the one with DMF, which was in CDCl₃.



Scheme 2.10 The formation of hypercoordinate complexes in the equilibria of RHSiCl₂ with nucleophiles.

NMI exceeded 1.2 equivalents suggested the cleaved Cl^- might be involved in a fast association process to have its charge to be partially neutralized internally, see **100**, **101**. Further increase of NMI would lead Cl to be substituted totally, see **102**, **103** and **104** and thus the conductivity kept rising. The titration of NMI or DMAP with MeHSiCl_2 also supported such suggestions. The titration of MeHSiCl_2 with DMF had practically no conductivity change, which was consistent with the the results from NMR study.of the mixture at room temperature.

$\text{MeHSiCl}_2 + \text{HMPA}$ (or DMPU)

The NMR study of the interactions between RHSiCl_2 and nucleophiles with large steric demand presented a different picture indeed. The titrations of MeHSiCl_2 with HMPA and DMPU against silicon-29 chemical shifts are illustrated in Figure 2.26.

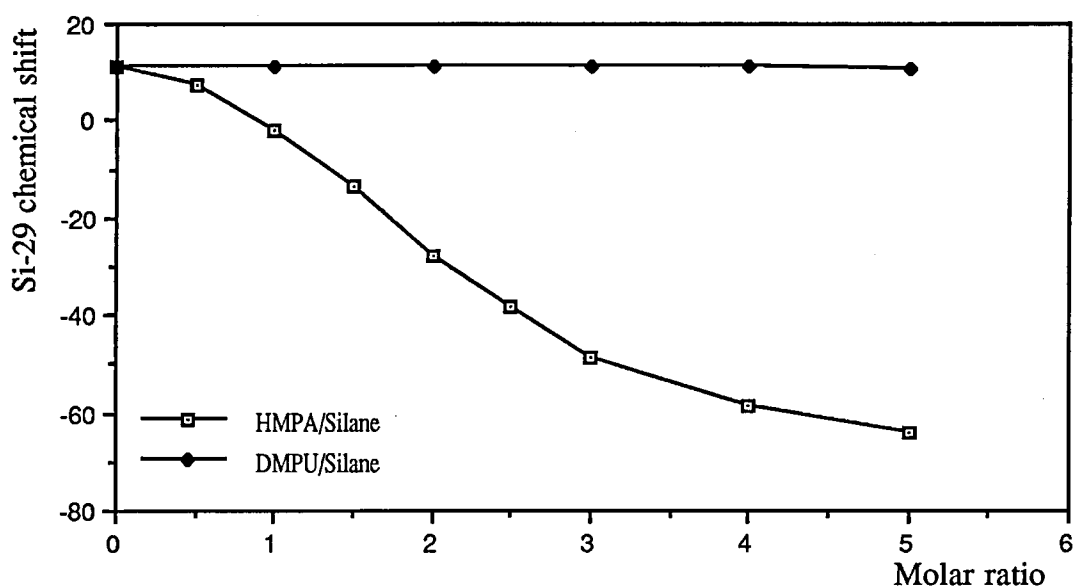


Figure 2.26 ^{29}Si NMR titrations of MeHSiCl_2 with HMPA and DMPU in CDCl_3 .

* $c = 0.5$ and 0.4 mmol./ml referred to MeHSiCl_2 respectively to HMPA and DMPU systems.

Adding HMPA, a strong nucleophile, into MeHSiCl_2 solution made the ^{29}Si resonance shift to high field progressively with broadened and diminishing signals. Nonetheless the $\delta^{29}\text{Si}$ values remained in the range of pentacoordinate silicon. The chemical shift

of silicon-29 observed at five equivalents of HMPA was -64 ppm with an increased ^{29}Si - ^1H coupling constant of 343.8 Hz. The protons of the MeHSi moiety were noticeably shielded. The chemical shifts moved gradually to high field with the increases of HMPA molar ratio from 5.59 (q) and 0.91 (d) ppm of the silane itself to 5.51 (s,br) and 0.76 (s, sbr) ppm at five equivalents of HMPA respective to the hydrogen and methyl groups of the MeHSi moiety. All these pieces of evidence suggested that pentacoordinate silicon species were the dominant components in the equilibria of MeHSiCl₂ with HMPA in solution.

NMR titration of MeHSiCl₂ with DMPU, a weak nucleophile, showed virtually no change of the chemical shifts of either ^{29}Si or ^1H , although an exothermic phenomenon was observed with the first addition of DMPU to the silane. The slightly broadened signals at high DMPU:MeHSiCl₂ ratio could be attributed to the homogeneity of the solution as it became more and more viscous.

However, with higher concentration at low temperature, see Table 2.17, a very much broadened weak signal of silicon-29 was observed with MeHSiCl₂ + 5 DMPU in CD₃CN. The high field shifted $\delta^{29}\text{Si}$ value of -53 ppm was also in the range of pentacoordinate silicon. The protons were deshielded at this low temperature as well. The changes of chemical shifts with temperature indicated that there were chemical equilibria between MeHSiCl₂ and DMPU, most likely forming pentacoordinate silicon complexes.

The chemical shift of silicon-29 of the mixture of MeHSiCl₂ with 5 HMPA shifted to higher field as the temperature was lowered. However there was only about a 14 ppm high field shift from 300 K to 222 K with a increased signal size and less broadening shape. This indicated that the resonance of silicon-29 of the mixture would reside within the range of pentacoordinate silicon ultimately.

PhHSiCl₂ + HMPA (or DMPU)

The interactions of PhHSiCl₂ with HMPA and DMPU in solution were similar to

Table 2.17 NMR data of the mixtures of $\text{RHSiCl}_2 + r \text{ Nu}$ at various temperatures.

	MeHSiCl_2				PhHSiCl_2			
	5HMPA (c=0.5)*		5DMPU (c=1.2)		6HMPA (c=0.5)		7DMPU (c=0.4)	
Temp.	300(K)	222K	300K	225K	300K	223K	300K	223K
$\delta^{29}\text{Si}$	-64.02 (br)	-78.52 (sbr)	Null	-53 (vbr)	-82.2 (sbr)	-96.3 (sbr)	-2.39	Null
$J_{\text{Si-H}}$	343.8	nr	Null	nr	334.1	339.9	300.4	Null
$\delta^1\text{H}$								
(HSi)	5.51(br)	nr	5.57	5.87	nr	5.78	5.98	6.00
(RSi)	0.76 (sbr)	nr	0.94(d)	0.95	7.68, 7.44	7.66, 7.40	7.69, 7.54	7.73, 7.56
(Nu)	2.75, 2.64	nr	3.20(t), 2.81, 1.91(qu)	3.28(t), 2.87, 1.94(qu)	2.71, 2.60	2.68, 2.57	3.18(t), 2.90, 1.96(qu)	3.28(t), 2.92, 1.98(qu)

* The concentrations referred to the silane; all were in CDCl_3 except MeHSiCl_2 with 5 DMPU, which was in CD_3CN .

those of MeHSiCl_2 , see Table 2.17. The mixture of PhHSiCl_2 with six equivalents of HMPA displayed a slightly broadened silicon-29 signal at high field with an increased coupling constant of $^{29}\text{Si}-^1\text{H}$. The ^{29}Si chemical shift value of -82.2 demonstrated that the dominant species in the equilibria was a pentacoordinate silicon adduct. The protons of the PhHSi moiety were increasingly shielded as well. Lowering the temperature of the sample enhanced such tendencies.

The mixture of PhHSiCl_2 with seven equivalents of weak nucleophile DMPU again showed no major chemical interaction when observed at room temperature by NMR. Nonetheless at low temperature the disappearance of the silicon-29 NMR signal and

the slightly increased shielding of protons, including the increase of the separation between the two sets of multiplets of phenyl group from 0.15 to 0.17 ppm, indicated there existed chemical equilibria in the mixture, probably resulting in pentacoordinate silicon complexes resembling those of MeHSiCl₂ with DMPU.

On the whole, the interactions of R₂HSiCl₂ (R = Me, Ph) with space demanding nucleophiles HMPA or DMPU examined by NMR in solution produced no evidence of hexacoordinate silicon complexes but did indicate pentacoordinated silicon. No disproportionation reaction of the pentacoordinate adducts, as in the case of [MeHSiCl₂-DMAP], was observed either. This possibly resulted from the equatorial position of the Si-H bonds within the pentacoordinate [R₂HSiCl₂·n HMPA] and [R₂HSiCl₂·n DMPU] adducts as their ²⁹Si-¹H coupling constants were greatly increased rather than decreased as in the case of [MeHSiCl-DMAP]. Therefore steric effects would affect not only the coordination number at silicon but also the reactivity of the adducts where pseudorotation was crucial.

Conductivity studies, MeHSiCl₂ + HMPA (or DMPU)

Conductivity titration studies of MeHSiCl₂ with HMPA or DMPU in CH₃CN + CHCl₃ showed HMPA increased the conductivity of the solution significantly while DMPU only had limited effect, which matched the weak interaction between them at room temperature. The titration curves were illustrated in Figure 2.27. Interestingly, the large increases of conductivity with HMPA were not at the beginning of the addition of HMPA but after nearly one equivalent HMPA added. This indicated the initial interaction between MeHSiCl₂ and HMPA was HMPA weakly associated to the silane to form pentacoordinate complexes without separate ions being produced. The cleavage of Si-Cl bonds, marked by the large increases of conductivity of the solution, took place within the pentacoordinated intermediate. To substitute the second chlorine from the pentacoordinate complex could be difficult and slow because of the steric hindrance of HMPA group to pseudorotation, which corresponded to the slow increases of conductivity when the amount HMPA was more than three equivalents.

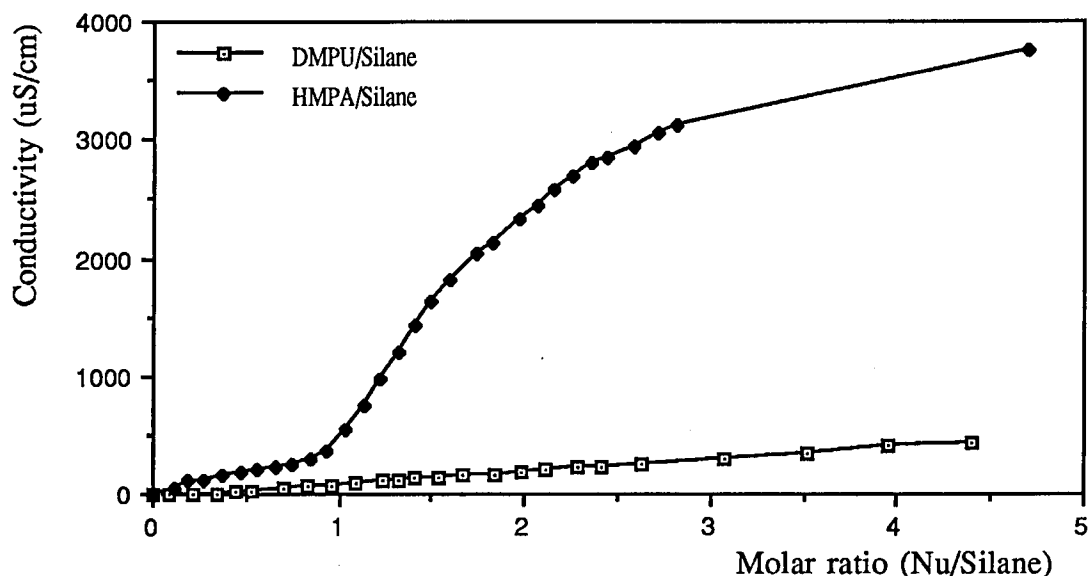
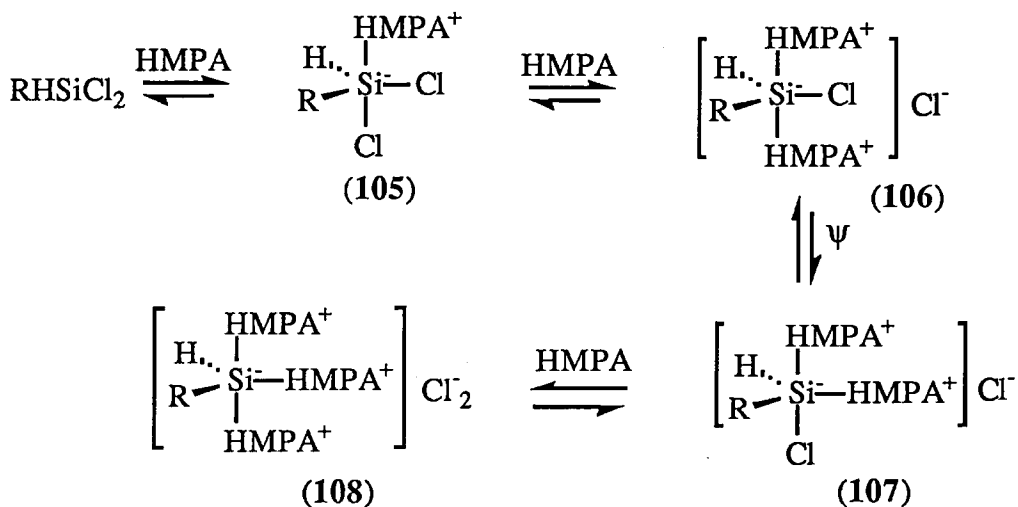


Figure 2.27 Conductivity titrations of MeHSiCl_2 with HMPA and DMPU.

The concentrations were 0.2 and 0.3 mmol./ml for HMPA and DMPU titration in $\text{CH}_3\text{CN} + \text{CHCl}_3$.

Therefore, the interactions of RHSiCl_2 with space demanding nucleophiles, represented by MeHSiCl_2 with HMPA, can be expressed by the following scheme (Scheme 2.11):



Scheme 2.11 Pathways of the interaction of RHSiCl_2 with space demanding nucleophiles.

2.4.2 The interactions of RHSiOTf_2 ($\text{R} = \text{Me, Ph}$) with nucleophiles

The interactions of RHSiOTf_2 with nucleophiles were, on the whole, more exothermic than with the corresponding chloride. The reaction mechanisms are again discussed according to the possible steric hindrance of the nucleophiles.

$\text{MeHSiOTf}_2 + \text{OTf}^-$

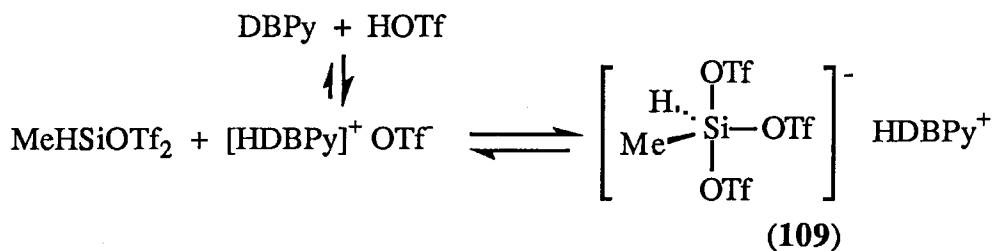
RHSiOTf_2 has much stronger tendency to increase coordination number at silicon than R_2HSiOTf . MeHSiOTf_2 would react even with OTf^- , a very good leaving group but poor nucleophile { produced by the interaction of triflic acid with 2,6-di-*tert*-butylpyridine (DBPy)}, to result in a pentacoordinate complex. Under similar conditions Me_2HSiOTf was practically inert to OTf^- , see Table 2.19. The high field shift of silicon-29 of the mixture of MeHSiOTf_2 with DBPy and HOTf in CDCl_3 from -9.5 to -67 ppm, together with the changes of ^{29}Si - ^1H coupling constant and chemical shifts of ^{13}C and ^1H ,

Table 2.19 NMR data for the interactions of $\text{Me}_n\text{HSiOTf}_{3-n}$ with OTf^- ($n = 1, 2$).

	MeHSiOTf_2		Me_2HSiOTf	
	DBPy	DBPy + HOTf	DBPy	DBPy + HOTf
$\delta^{29}\text{Si}$ (ppm)	-9.49	-66.98	25.13	23.43
$J_{\text{Si-H}}$ (Hz)	306.6	351.6	235.3	238.3
$\delta^{13}\text{C}$ (ppm)	1.78	4.88	-1.32	-1.07
$\delta^1\text{H}$ (ppm) (RHSi)	5.32(q), 0.95(d)	5.26(sbr), 0.76(sbr)	4.95(mt), 0.57(d)	4.93(mt), 0.58

* The concentrations were 0.4 mmol./ml for MeHSiOTf_2 in CDCl_3 and 1.2 mmol./ml for Me_2HSiOTf in CD_3CN .

clearly demonstrated the formation of pentacoordinate species **109** see Scheme 2.12.



Scheme 2.12 Interaction of MeHSiOTf₂ with OTf⁻.

MeHSiOTf₂ + NMI

NMR examination of the interaction of MeHSiOTf₂ with NMI showed no interference from the cleaved OTf⁻ groups. The NMR titration data were collected in Table 2.20.

Interestingly, the high field shifts of silicon-29 of the mixture with the additions of NMI were not straight forward but had a sharp drop at about two equivalents of NMI. Compared with the $\delta^{29}\text{Si}$ value of -66.98 ppm for [MeHSiOTf₃]⁻ (**109**), it was reasonable to believe that the high field shifted ²⁹Si chemical shift of -66.10 ppm with one equivalent of NMI corresponded to a pentacoordinate silicon complex in which the NMI was directly associated with MeHSiOTf₂. The sudden drop of $\delta^{29}\text{Si}$ value to the range of tetracoordinate silicon of -34 ppm at two equivalents of NMI, together with the increased deshielding of protons of NMI and decreased separation between the protons of C₄ and C₅, indicated that the pentacoordinated adducts collapsed to tetracoordinated adducts, with double displacement of the triflate groups by NMI. The continued high field shifts of ²⁹Si resonance with further increases of NMI molar ratio to -95 ppm with very weak and broadened signal at three equivalents of NMI and to -169.7 ppm with strong and sharp signal at four equivalents of NMI suggested that the doubly substituted adducts [MeHSiNMI₂]⁺ OTf₂⁻ coordinated extra NMIs to form hexacoordinate silicon complexes [MeHSi²⁺-NMI₄]⁺ OTf₂⁻. These hexacoordinate complexes were quite stable as the effects of the concentration of the adducts and the

Table 2. 20 NMR data of the mixtures of MeHSiOTf₂ with r NMI.

r	c*	T (K)	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}$ (ppm)		
					HSi	MeSi	NMI
0		300	-13.99	328.1	5.27(q)	0.93(d)	(7.37, 6.96, 6.85, 3.53)
1	0.65	300	-66.10	331.2	5.56(q)	0.94(d)	8.58, 7.50, 7.39, 3.92
2	0.65	300	-34.08	329.7	5.86(q)	0.94(d)	8.77, 7.48, 7.46, 3.91
3	0.65	300	-95(vbr)	338.5	6.00(sbr)	1.16(d)	8.52, 7.29, 7.27, 3.85
4	0.65	300	-169.74	338.5	5.81(sbr)	1.24(sbr)	8.32, 7.21(sbr), 3.77
	0.16	300	-169.90	338.5	5.78(sbr)	1.22(sbr)	8.30, 7.23(br), 3.82
	0.16	225	-171.47	336.5	5.77(sbr)	1.23(sbr)	8.36(br), 7.26(br), 3.84
5	0.65	300	-169.83	338.5	5.83(sbr)	1.26(sbr)	8.20, 7.19(sbr), 3.78

The concentrations were in mmol./ml in CD₃CN + CDCl₃.

temperature of the sample were very limited. However, there were exchanges between the associated and free NMI, marked by the single set of resonances attributable to NMI at a molar ratio of 5:1 NMI to MeHSiOTf₂. Solid adducts isolated were also found to have the formula of MeHSiOTf₂·4 NMI by elemental analysis.

PhHSiOTf₂ + NMI

The interaction of PhHSiOTf₂ with NMI observed by NMR, see Table 2.21, were also found to associate NMI to form pentacoordinate adducts initially and to produce substituted hexacoordinate complexes finally. The direct association of NMI to silicon was clearly demonstrated by the two ²⁹Si resonance signals with nearly equal

Table 2.21 NMR data of the mixtures of PhHSiOTf₂ with r NMI.

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}(\text{ppm})$		
			HSi	PhSi**	NMI
0	-28.20	323.2	5.69	7.74, 7.64	(7.37, 6.96, 6.85, 3.53)
0.5*	-33.42	322.4	5.69	7.73,	8.39, 7.45, 7.21, 3.82(br)
	-86.02(sbr)	370.7	6.09	7.61(br)	
1.0	-89.73	372.1	6.07	7.67(br)	8.39, 7.43, 7.24, 3.81
1.5	-77.22(sbr)	335.6	6.27	7.73,	8.51, 7.48, 7.42, 7.20, 3.89(s), 3.86, 3.78(s)
	-89.73	375.1	6.06	7.57(br)	
2.0	-74.50(sbr)	337.1	6.32(br)	7.58(br)	8.50, 7.49, 7.19, 3.86(br)
3.0	-114.84(s, br)	329.7	6.43	7.49(br)	8.24, 7.23, 7.00, 3.82
4.0	-170.90(sh)	341.4	6.20	7.41(br)	8.10, 7.09, 6.91, 3.78
5.0	-171.06	344.4	6.20	7.41(br)	7.98, 7.06, 6.91, 3.74

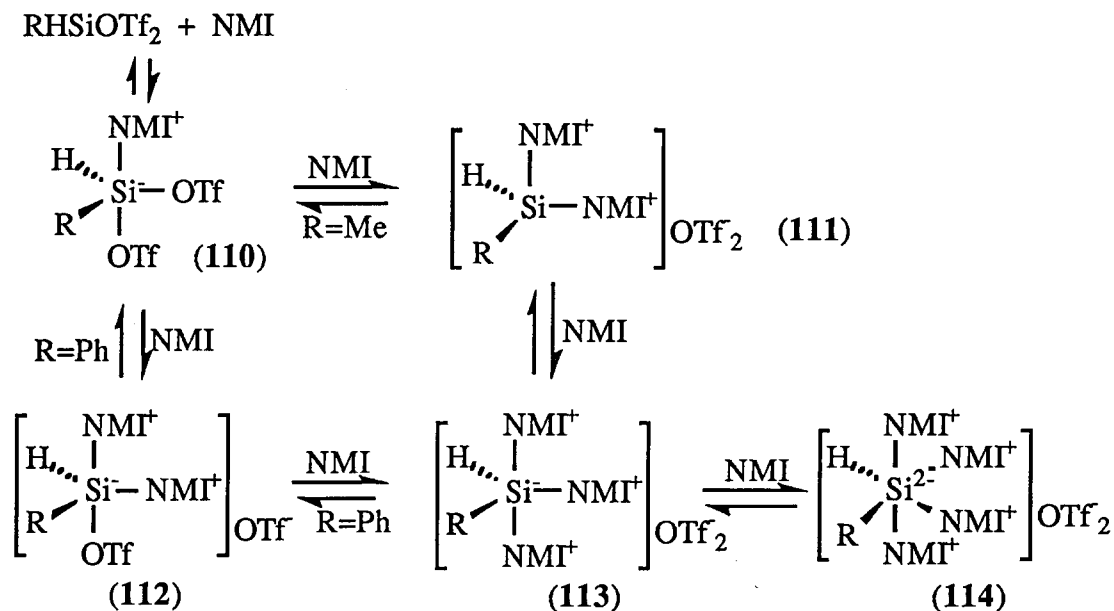
* c = 0.8 mmol./ml in CD₃CN + CDCl₃.

** The proton signals of phenyl group were overlapped in some cases.

intensity at 0.5 equivalents of NMI; the one at low field with the unchanged ²⁹Si-¹H coupling constant and proton shifts of the PhHSi moiety and the other one at high field with an increased ²⁹Si-¹H coupling constant and deshielded Si-H proton correspond to an equilibrium between the silane itself and a pentacoordinate silicon complex. The single sharp ²⁹Si signal at -171 ppm was a sign of hexacoordinate silicon. With PhHSiOTf₂, however, further interaction of NMI with the initially formed

pentacoordinate complex did not collapse the pentacoordinate structure. At 1.5 equivalents of NMI, the additional ^{29}Si signal at -77.2 ppm, nearly a 50 ppm high field shift from that of MeHSiOTf_2 and being in the range of pentacoordinate silicon, in addition to the one at -89.7 ppm belonging to $[\text{PhHSi}^-\text{OTf}_2(\text{NMI}^+)]$ and the large separation of proton signals, together with the broadened ^{29}Si and ^1H signals at two equivalents of NMI, suggested a substitution of a triflate group took place within the pentacoordinate structure to produce a monosubstituted complex $[\text{PhHSi}^-\text{OTf}(\text{NMI}^+)_2]\text{OTf}^-$. This differs from MeHSiOTf_2 , in which $[\text{MeHSi}(\text{NMI}^+)_2]$ is the stable species at a 2:1 ratio, probably because the phenyl group is more electron-withdrawing and can offset the charges in the molecule better than the methyl group. Therefore the interaction of PhHSiOTf_2 with NMI at early stages gives a good example for the nucleophilic substitution at silicon by five-coordinate intermediates.

The pathways of the interactions of RHSiOTf_2 with NMI can be generally expressed in Scheme 2.13. The formation of pentacoordinate species **110** with one equivalent of NMI and the hexacoordinate complex **114** with four NMIs were common to both, though the methyl silane favoured tetracoordinate intermediate **111** and the phenyl silane could



Scheme 2.13 Reaction pathways of RHSiOTf_2 with NMI

maintain five-coordinated structure **112**. Intermediate **113** was not seperably observed for either silane for the life time of that species was too short on the NMR time scale resulting from fast exchanges.

RHSiOTf₂ + DMAP (or DMF)

DMAP interacted with RHSiOTf₂ in a similar way of those of NMI with MeHSiOTf₂ but DMF catalyzed a disproportionation reaction of the silanes. Some typical NMR data of the mixtures are listed in Table 2.22.

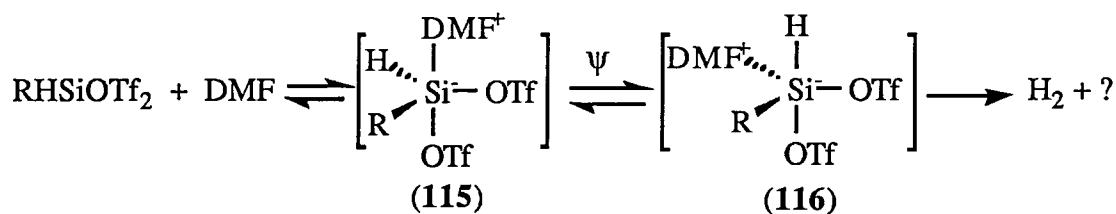
Silicon-29 NMR data showed that the interactions of DMAP with MeHSiOTf₂ or PhHSiOTf₂ were very much alike. DMAP would firstly associate to silicon to increase its coordination number to five without substitution of the triflate group, then these pentacoordinate complexes collapsed to form the doubly substituted tetracoordinate adduct. Hexacoordinated species were produced with further increase of DMAP molar ratios, though the shielding effect on silicon of DMAP was less than that of NMI. The only differences were the exchange rate involving the pentacoordinate intermediates [RHSi⁻(DMAP⁺)₃] OTf₂ equivalent to **113** and other complexes. It was found that the pentacoordinate equivalent to **113** for the phenyl silane was in faster exchange than that of the methyl silane as a high field shielding ²⁹Si signal for the former could be followed with increases of DMAP molar ratio while the latter had null signal around three equivalents of DMAP (not listed in Table 2.22). Therefore Scheme 2.13 for the interaction of RHSiOTf₂ with NMI can be expanded to include DMAP.

The fact that the weak nucleophile DMF catalyzed an oxidation reaction of RHSiOTf₂ was obvious as the ²⁹Si-¹H coupling and Si-H proton signal were lost in both ²⁹Si and ¹H NMR spectra and gas was produced during the time the samples were run. These can be expressed in Scheme 2.14. Presumably the Si-H bond was activated by coordination DMF to silicon forming a pentacoordinated intermediate, marked by the deshielded protons of DMF, with the Si-H bond in an axial position.

Table 2.22 NMR data for the interactions of R₂HSiOTf₂ with DMAP and DMF.

Silane	MeHSiOTf ₂				PhHSiOTf ₂			
Nu	r DMAP		r DMF		r DMAP		r DMF	
r	2.3	6.0	1.0	3.0	1.7	5.0	1.0	3.0
c*	0.7	0.2	0.6	0.6	0.7	0.2	0.9	0.9
δ ²⁹ Si	-2.06(s) -53.76	-135.66	Null	-164.3	-79.4(s) -37.54	-124.63	Null	-175.67
J _{Si-H}	303.3(s) 345.8	345.8	Null	5.9	320.9(s), 360.5	345.8	Null	6.9
δ ¹ H (SiH)	5.51(s) 5.79	5.36	5.29	Null	6.24(s) 6.04	5.89	5.71	Null
(SiR)	1.00(s) 1.29	1.16	0.88(d)	0.29	7.54(mt)	7.44, 7.38	7.73(mt) 7.51(mt)	7.3(br)
(Nu)	8.04(d) 6.99(d) 3.26 (all s) 8.21(d) 6.96(d) 3.24	8.01(d) 6.65(d) 3.08	8.33 3.38(d) 3.24(d)	8.32 3.26 3.18	8.05(mt) 6.94(mt) 3.16(s) 3.22	7.90(d) 6.62(d) 3.10	8.23 3.27(s) 3.18	8.19 3.33 3.16

The concentrations were in mmol./ml in CD₃CN + CDCl₃.



Scheme 2.14 Interaction of RHSiOTf_2 with DMF.

Conductivity studies, $\text{RHSiOTf}_2 + \text{NMI}$

The conducting properties of the mixtures of RHSiOTf_2 with NMI in solution were consistent with the pathways illustrated in Scheme 2.13. The conductivity titration curves of RHSiOTf_2 with NMI, see Figure 2.28, showed that there was little increase

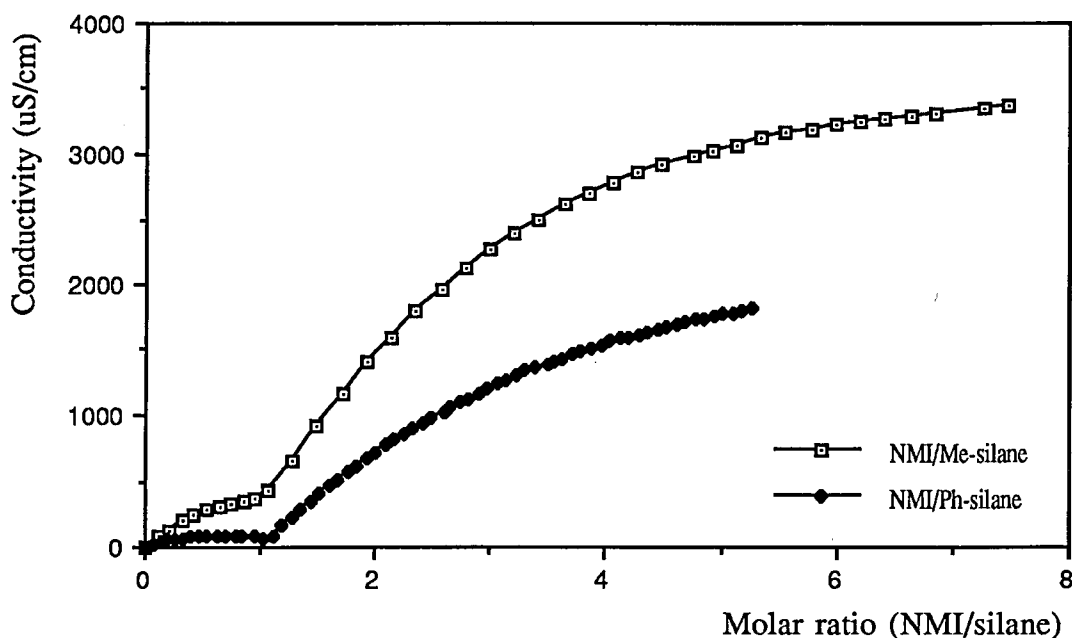


Figure 2.28 Conductivity titrations of RHSiOTf_2 with NMI in solution.

* $c = 0.16$ and 0.06 mmol./ml in $\text{CH}_3\text{CN} + \text{CHCl}_3$ for MeHSiOTf_2 and PhHSiOTf_2 respectively.

in the conductivity of the solutions when NMI was less than one equivalent of RHSiOTf_2 , which corresponded the formation of pentacoordinate species **110**. The large increases of conductivity of the solutions when NMI was present in more than one

equivalent indicated the production of ionic species **111** or **112** by substitution. Similar conductivity results were obtained with the reaction between RHSiOTf_2 and DMAP.

$\text{MeHSiOTf}_2 + \text{HMPA}$

The mechanism of nucleophilic reactions between RHSiOTf_2 and nucleophiles with initial pentacoordination and then collapse to tetracoordination is clearly demonstrated by the interaction of MeHSiOTf_2 with HMPA. Some typical NMR properties of the reaction mixtures are collected in Table 2.23.

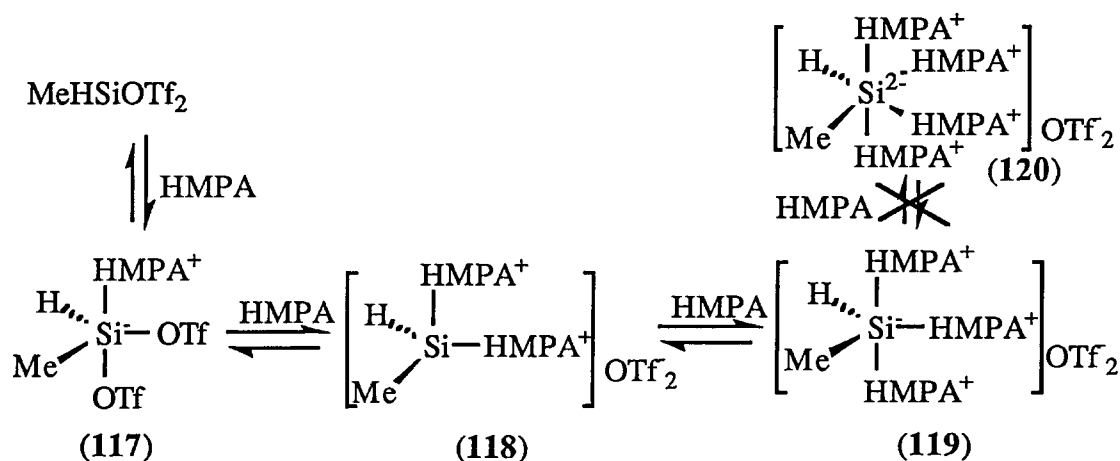
Table 2.23 NMR data of the mixtures of $\text{MeHSiOTf}_2 + r \text{ HMPA}$ in CDCl_3

r	0.9*	1.9	2.1	2.8	5.0	6.0
$\delta^{29}\text{Si}$	-61.58(d)	-23.48(t)	-24.19	-55.63	-72.25	-78.50
$J_{\text{Si-H}}$	345.9	300.4	299.8	300.8	327.1	330.1
$J_{\text{Si-P}}$	4.4	4.5	-	-	-	-
$\delta^{31}\text{P}$	26.82	27.76	27.66	25.71	24.90	24.47
$\delta^1\text{H}$ (HSi)	5.31	5.26	5.25	5.20	5.17	5.18
(MeSi)	0.78	0.86	0.86(d)	0.74	0.67	0.67
(HMPA)	2.85, 2.73	2.88, 2.76	2.86, 2.74	2.81, 2.70	2.79, 2.67	2.77, 2.66

* c = 0.8 mmol./ml relative to the silane in this table.

In the ^{29}Si NMR spectra, the resonances shifted firstly to high field (-61.58 ppm) then to low field (-23.48 ppm) and then high field again (up to -78.5 ppm) as the amount of HMPA increased and the coupling of ^{29}Si with ^{31}P around one and two equivalents of HMPA was also recorded. The doublet at -61.58 ppm and the triplet at

-23.48 ppm corresponded to a pentacoordinated silicon bonded to one HMPA and a tetracoordinated silicon bonded to two HMPAs. The high field shift with collapse of the ^{29}Si - ^{31}P coupling signals when more HMPA added suggested a pentacoordinate complex produced in the equilibrium together with a fast exchange between the free HMPA and those bonded to silicon. There is no evidence of the formation of hexacoordinate silicon as the signals at five and six equivalents of HMPA were nearly natural width with narrowed shift span. The increased coupling constant of ^{29}Si - ^1H of the ^{29}Si signals at high field, according to Tandura³⁵, showed that the Si-H bond was equatorial. The changes of the coupling constant of ^{29}Si with ^1H and the chemical shifts of ^{31}P and protons verify this interpretation. The reaction process is summarized in Scheme 2.15.



Scheme 2.15 Progress of the reaction of MeHSiOTf₂ with HMPA.

PhHSiOTf₂ + HMPA

The interaction of PhHSiOTf₂ with HMPA observed by NMR is very similar to that of MeHSiOTf₂ (see Table 2.24). The changes in silicon-29 NMR, as well as those of ^{31}P and protons, of the mixtures of PhHSiOTf₂ + r HMPA almost have the same pattern of those of MeHSiOTf₂. The only exception is that the phenyl silane had

Table 2.24 NMR data of the mixtures of PhHSiOTf₂ + r HMPA in CD₃CN + CDCl₃.

r	0.5	1.1	1.8	2.5	5.0	6.5
$\delta^{29}\text{Si}$	-53(br) -65(br)	-82.48 (sbr)	-38.5 (vbr)	-46.02 (sbr)	-93.56	-98.13
$J_{\text{Si-H}}$	329.7 337.1	344.4	296.0	300.4	339.9	347.2
$\delta^{31}\text{P}$	27.23(sbr)	26.05	28.57	27.93	25.85	25.64
$\delta^1\text{H}$						
(HSi)	5.72	5.77	5.68	5.65	5.64	5.64
(PhSi)	7.68, 7.54 (br)	7.68, 7.46	7.83, 7.67	7.80, 7.67	7.58 (br)	7.34 (br)
(HMPA)	2.78, 2.66	2.81, 2.69	2.80, 2.68	2.77, 2.65	2.71, 2.60	2.71, 2.60

* c = 0.4 mmol./ml relative to the silane.

broadened signals together with the loss of ^{29}Si - ^{31}P coupling with low molar equivalents of HMPA ($r < 0.5$) because of the quite fast exchange between the pentacoordinate adducts and the tetracoordinated silicon. That means the intermediates of PhHSiOTf₂ with HMPA, equivalent to **117** and **118**, are more labile than those from the methyl silane. Nonetheless the scheme for the interaction of MeHSiOTf₂ with HMPA (Scheme 2.15) can be equally applied to the reaction of PhHSiOTf₂ with HMPA. Hexacoordination, equivalent to **120**, was again not found.

RHSiOTf₂ + DMPU

The process observed by ^{29}Si and ^1H NMR spectra of the reactions of RHSiOTf₂ (R = Me, Ph) with the weak and spacially demanding nucleophile DMPU is the same as that of RHSiOTf₂ with strong nucleophile HMPA. Some typical NMR data are listed in Table 2.25 and Table 2.26.

Table 2.25 NMR data for the mixtures of MeHSiOTf₂ + r DMPU.

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}$ (ppm)		
			HSi	MeSi	DMPU
0	-7.74	306.6	5.30(qu)	0.95(d)	(3.26, 2.89, 1.98)
1.0	-68(vbr)	354.	5.22(qu)	0.79	3.50, 3.14, 2.14(sbr)
2.0	-34(vbr)	319.	5.36(sbr)	0.88	3.56(t), 3.14, 2.14
3.0	-53.92(sbr)	326.7	5.36	0.77	3.50, 3.07, 2.09(sbr)
4.0	-70.06	328.3	5.35	0.69	3.45(t), 3.03, 2.07(sbr)

* c = 0.8 mmol./ml relative to the silane in CDCl₃.

Table 2.26 NMR data for the mixtures of PhHSiOTf₂ + r DMPU.

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}$ (ppm)		
			HSi	MeSi	DMPU
0	-28.20	323.2	5.69	7.74, 7.64	(3.26, 2.89, 1.98)
0.5	-30.29(sbr)	320.9	5.71	7.75(br)	3.45, 3.06, 2.02(br)
	-85.37(sbr)	334.0	(sbr)	7.48(br)	
1.0	-92.69	338.4	5.72	7.80, 7.44	3.44, 3.05, 2.08(sbr)
2.0	-61.16(br)	344.4	5.82	7.80, 7.54	3.50, 3.07, 2.07(br)
3.0	-86.44	339.9	5.72	7.50(vbr)	3.40, 2.98, 1.98(br)
4.0	-92.77	336.8	5.71	7.48(vbr)	3.37, 2.96, 1.97(br)
5.0	-93.85	335.5	5.71	7.48(vbr)	3.34, 2.94, 1.96(br)

* c = 0.5 mmol./ml relative to the silane in CDCl₃.

The ^{29}Si resonances within the range of pentacoordinate silicon were observed with one equivalent DMPU added to either MeHSiOTf_2 or PhHSiOTf_2 in solution. In the presence of two equivalents of DMPU, once again, the $\delta^{29}\text{Si}$ values in both cases shifted back to the range of tetracoordinate silicon. The progressively high field shifts with more DMPU added thereafter indicate the production of pentacoordinate complexes in the equilibria. No evidence of the existence of hexacoordinate silicon was found. Therefore the scheme developed for the interaction of MeHSiOTf_2 with HMPA (Scheme 2.15) also apply to the reactions of RHSiOTf_2 with DMPU.

Conductivity studies, $\text{RHSiOTf}_2 + \text{HMPA}$ (or DMPU)

The titrations of RHSiOTf_2 ($\text{R} = \text{Me, Ph}$) with either HMPA or DMPU against conductivity of the mixture solutions have also showed an initial formation of neutral pentacoordination as no significant conductivity were observed with small equivalents of the nucleophiles (see Figure 2.29). There were points of inflexion in the titration

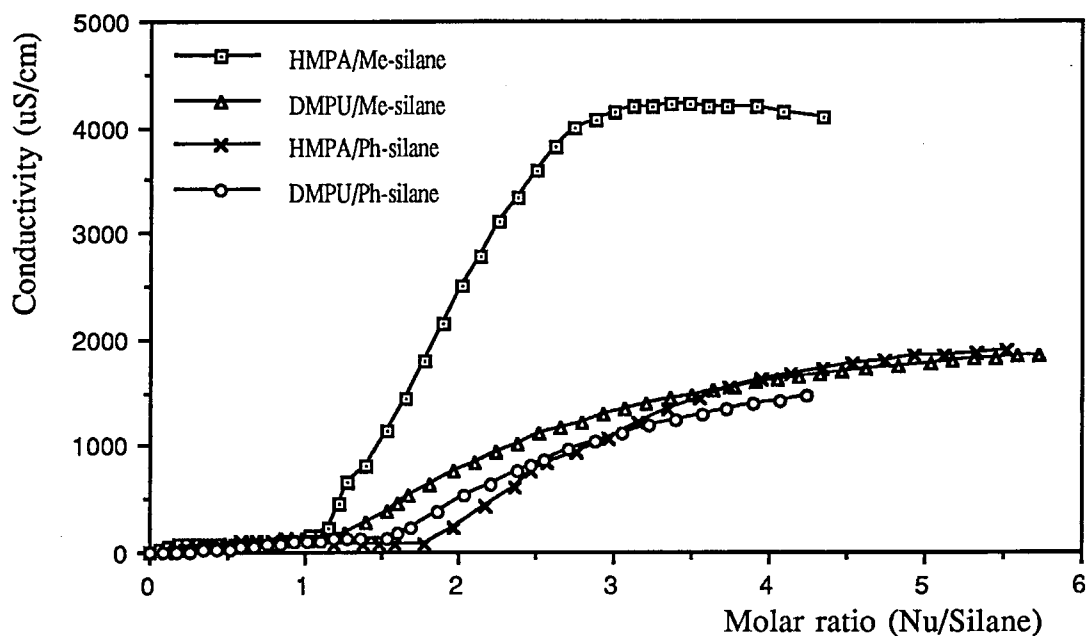


Figure 2.29 Conductivity titrations of RHSiOTf_2 with either HMPA or DMPU.

* $c = 0.10, 0.17, 0.09$ and 0.10 mmol./ml relative to the silanes for HMPA and DMPU titrating MeHSiOTf_2 and PhHSiOTf_2 respectively. The titration were done in CHCl_3 except HMPA/ MeHSiOTf_2 , which was carried out in a mixed solvent $\text{CH}_3\text{CN} + \text{CHCl}_3$.

curves, though they were not at the exact molar ratios perhaps because of an error in the quantitative measurements of the silane (see Chapter 7) and the interference from the solvent, especially those in CHCl_3 . However these curves displayed nearly the same character of conductivity, which agrees with the reaction mechanism representatively illustrated in Scheme 2.15.

2.4.3 Summary

NMR studies of the interaction of RHSiX_2 ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{Cl, OTf}$) with neutral nucleophiles together with the results of conductivity and analysis of solid adducts have showed that a replacement of the alkyl group from R_2SiX_2 ($\text{R} = \text{Me, Ph}$) by hydrogen leads to changes in the reaction mechanism and the coordination of the final adducts.

The coordination

RHSiX_2 has a much stronger tendency to increase its coordination at silicon than R_2SiX_2 . The ultimate adducts of RHSiX_2 with nucleophiles have a coordination number one greater than those of R_2SiX_2 . Both penta- and hexa-coordinated complexes as final adducts of the interactions of RHSiX_2 with nucleophiles are observed. Tetra-, penta- and in some cases hexa-coordinate intermediates exist in the equilibria.

The nucleophiles with less steric hindrance Nu^{I} , including NMI, DMAP and DMF, will ultimately produce hexacoordinate silicon complexes while more spacially demanding nucleophiles Nu^{II} , including HMPA and DMPU, form adducts with coordination number never exceeding five. As a matter of fact, the final products of RHSiX_2 and Nu^{II} are always pentacoordinated at silicon.

The pathway

The reaction pathways of RHSiX_2 with nucleophiles are different from those of R_2SiX_2 and are very much dependent on the nature of nucleophile and the leaving

group as well as the R group. The most likely mechanisms are presented in Scheme 2.16 on the next page.

The nucleophilic reaction mechanisms of RHSiX_2 can be divided into two main pathways according to whether the nucleophile can form hexacoordinated silicon complexes. They are so complicated that it is no wonder that the nucleophilic reaction mechanisms of silanes proposed in the literature are so diverse. Although quite a few structures of the intermediates in the two main pathways are the same, say **121** / **128**, **123** / **129**, **124** / **130** and **125** / **131**, they develop differently according to the nucleophiles, the leaving groups and the R groups.

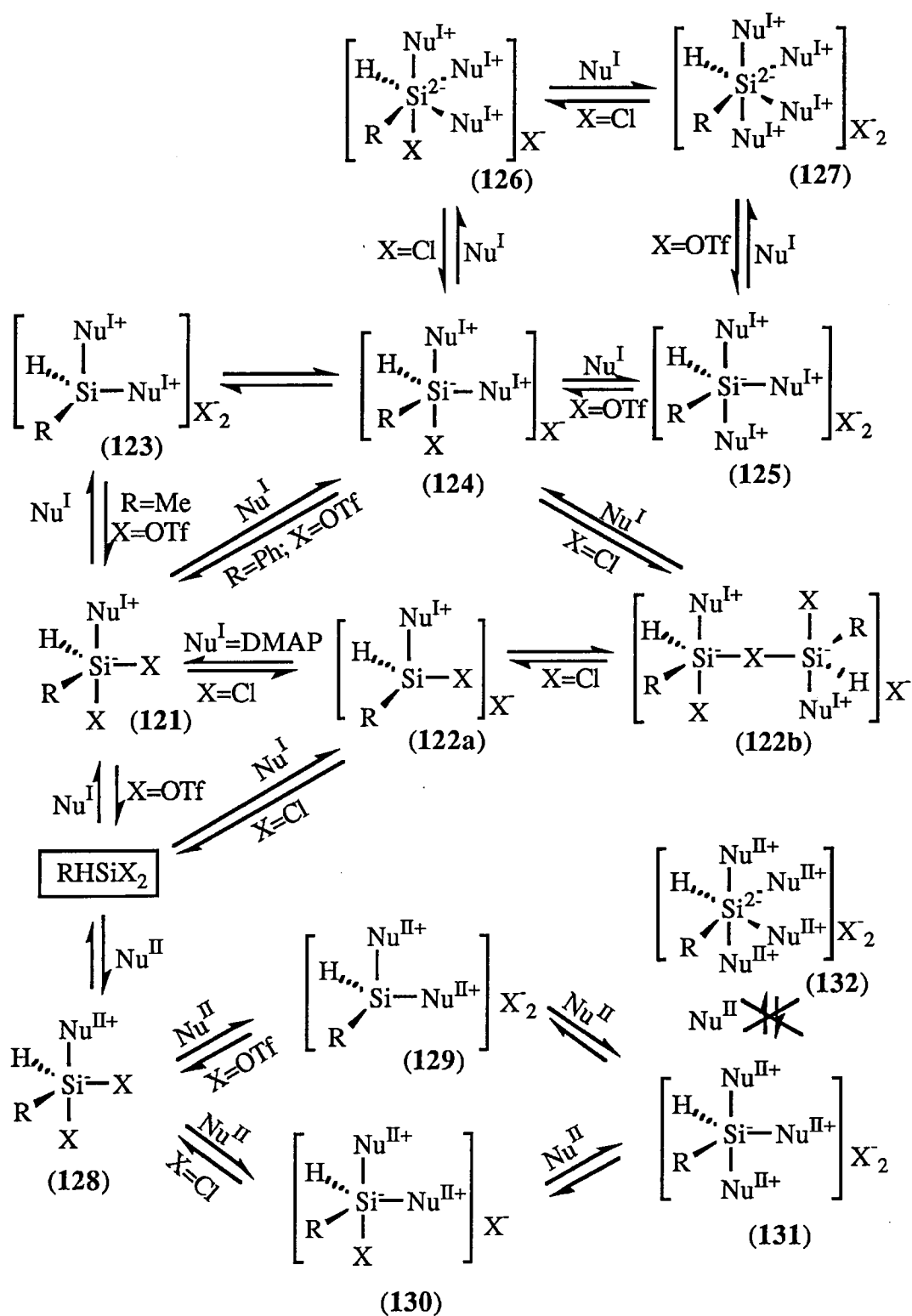
The nucleophile

The steric size of the nucleophile determines the highest coordination number at silicon. This probably results from the possible steric crowding upon complexation of the nucleophile. The nucleophilicity of the nucleophile contributes only to the equilibrium constants of the reactions of the same category of nucleophiles. Generally speaking, the larger the nucleophilicity (Taft's Beta value), the greater the equilibrium constant K for a particular reaction or reactions of the same mechanism.

The steric hindrance from the nucleophile may also contribute to the pseudorotation energy within the pentacoordinate complexes. A disproportionation reaction of MeHSiCl_2 with DMAP and a decomposition reaction of RHSiOTf_2 with DMF were observed possibly by pseudorotation of **121** to place Si-H bond at an apical position as required if the hydrogen atom behaves as a leaving group. Such reactions were not found with spacially demanding nucleophiles Nu^{II} .

The leaving group

The leaving ability and the basicity of the leaving group cooperate in building up various intermediates. Chloride, as a poorer leaving group than triflate, tends to maintain the Si-Cl bond and thus leads to extracoordination at silicon, such as **121**,



Nu^I: NMI, DMAP, DMF

Nu^{II}: HMPA, DMPU

Scheme 2.16 Nucleophilic reaction mechanisms of RHSiX₂.

122b, 124, 126, 128 and 130. However, substitution also occurs to give tetracoordinate species such as **122a**.

By contrast with the interactions of Me_2HSiOTf with nucleophiles, in which a substitution process comes first^{51, 102}, the reaction of RHSiOTf_2 with nucleophiles always forms pentacoordinate complexes **121** or **128** in the first step. This intermediate will collapse into doubly substituted tetracoordinate adducts **123** or **129** with further nucleophilic attack. More nucleophilic groups can be associated with these adducts to constitute hypercoordinate species, such as **125, 127** and **131**.

The R group

The presence of either a methyl or a phenyl group as R in RHSiX_2 will not affect the coordination at silicon in the reactions. Presumably their steric hindrance is not so different compared with hydrogen. However, the phenyl group has a better ability to stabilize the charges accumulated in the complexes, which leads the phenylsilane species to be more reactive. That means the intermediates from the phenylsilane are much more labile than those from the methylsilane. Therefore the ^{29}Si - ^{31}P coupling has not been observed with PhHSiX_2 and HMPA in any of the reactions examined. PhHSiOTf_2 has an intermediate **124** while MeHSiOTf_2 does not and so on. So the charge distribution and stabilization within the complexes are very important in both the coordination chemistry of silicon and the reaction mechanism of silicon compounds.

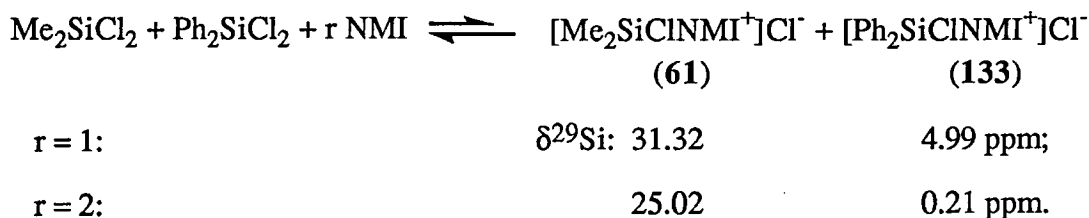
2.5 Reactivity of R_2SiX_2 and MeHSiX_2 (R = Me, Ph) with nucleophiles.

The reactivity of silanes is delicately balanced between the steric and electronic effects of the substituents. It is reported that the rate of hydrolysis and alcoholysis of chlorosilanes decreases with the number of chlorine atoms bonded to silicon^{80a}. The rate of substitution is also supposed to increase with decreases of steric hindrance^{80b}. As RHSiX_2 have been shown to be more ready to increase their

coordination with nucleophiles than R_2SiX_2 , it is interesting to observe their behaviour when they co-exist with nucleophiles.

$Me_2SiCl_2 + Ph_2SiCl_2 + NMI$

There is not much difference of the reactivities between Me_2SiCl_2 and Ph_2SiCl_2 towards nucleophiles. The $\delta^{29}Si$ NMR spectra showed, see Scheme 2.17, that

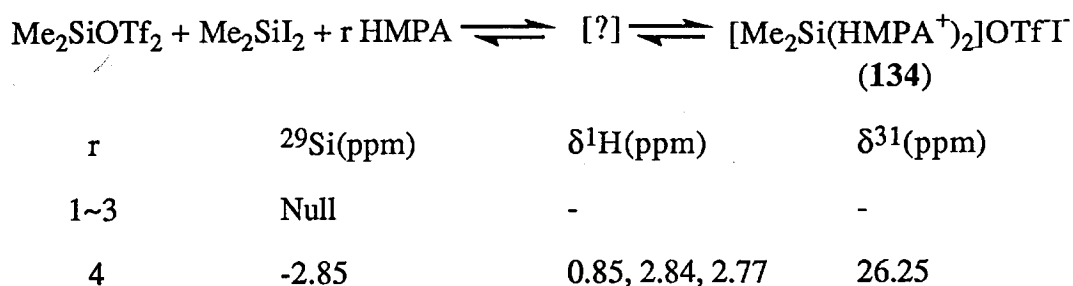


Scheme 2.17 competitive reactions of R_2SiCl_2 ($R = Me, Ph$) with NMI in $CDCl_3$.

the reactivity of Me_2SiCl_2 and Ph_2SiCl_2 towards NMI are of a similar order. Both slowly shifted to high field simultaneously upon addition of NMI, exchanging with monosubstituted adducts **61** and **133** respectively.

$Me_2SiOTf_2 + Me_2SiI_2 + HMPA$

The reactivity of a silane is much related to the leaving group. The leaving group can undergo exchange if more than two leaving groups co-exist in an equilibrium. The interaction of Me_2SiOTf_2 and Me_2SiI_2 with HMPA provided a good example as shown in Scheme 2.18. In the ^{29}Si NMR spectra, null signal was recorded when

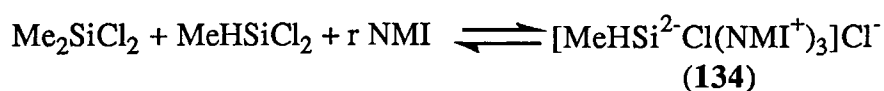


Scheme 2.18 Cooperation of leaving groups.in $CDCl_3$.

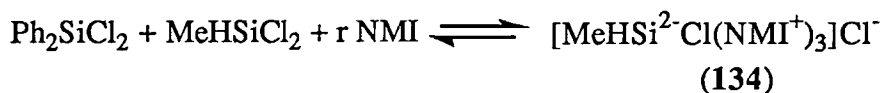
HMPA was less than three equivalents ($r \leq 3$). Presumably an intermediate exchange was going on, which was not observed with either silane individually. However, with four equivalents of HMPA a singlet appeared at -2.85 ppm together with single signals of the protons and ^{31}P and indicated the formation of adduct **134**. Similar exchange process was observed by NMR with the mixtures of Ph_2SiCl_2 and $\text{Me}_2\text{SiOTf}_2$ and NMI. In this way the reactivity of a silane with poor leaving groups can be improved.

$\text{R}_2\text{SiCl}_2 + \text{MeHSiCl}_2 + \text{NMI}$

The reactivity difference between R_2SiCl_2 and MeHSiCl_2 towards NMI is enormous as shown in Scheme 2.19. The ^{29}Si NMR signals of R_2SiCl_2 did not change at all



$r = 1$	$\delta^{29}\text{Si}(\text{ppm}):$ 32.75, Null
$r = 3$	32.86, -170.3(solids)



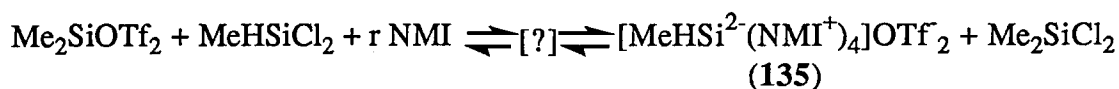
$r = 1$	$\delta^{29}\text{Si}(\text{ppm}):$ 5.9, Null
$r = 3$	5.1, -147 (vbr)

Scheme 2.19 Competitive reactions of R_2SiCl_2 and MeHSiCl_2 with NMI in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

while that of MeHSiCl_2 disappeared immediately after the initial addition of NMI and reappeared at a high field within the range of hexacoordinate silicon with three equivalents of NMI present, which indicates the formation of hexacoordinated complexes, such as **134**. The huge reactivity difference like this are useful in both chemical and physical applications.

MeHSiCl₂ + Me₂SiOTf₂ + NMI

The competitive interaction of Me₂SiOTf₂ and MeHSiCl₂ with NMI observed by NMR proved to be interesting, as shown in Scheme 2.20. With low equivalents of



r	$\delta^{29}\text{Si}(\text{ppm})$	$J_{\text{Si-H}}(\text{Hz})$	$\delta^1\text{H}(\text{ppm})$		
			HSi	MeSi	NMI
1	29.02, 26.28, 11.58*, 1.59, Null	8.8 296.7*	5.58, 5.61	0.84, 0.88, 0.81, 1.02	8.92, 8.65, 7.51, 7.34, 3.95(sbr)
3	Null		5.81	0.90, 1.05	8.62, 7.34, 3.89
4	32.35, -160.0(br)*	8.8 334.1*	5.80	0.83 1.20	8.42, 7.24, 7.14, 3.81

Scheme 2. 20 Competitive reaction of Me₂SiOTf₂ and MeHSiCl₂ with NMI and the NMR data in CD₃CN + CDCl₃.

* Corresponding data (The $\delta^{29}\text{Si}$ values of Me₂SiOTf₂, Me₂SiCl₂, MeHSiOTf₂ and MeHSiCl₂ are 16.4, 32.3, -13.9 and 11.4 respectively).

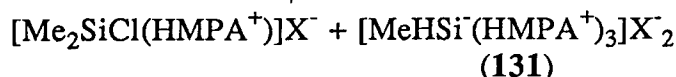
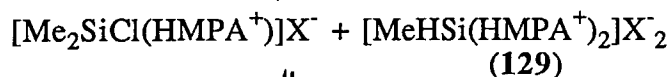
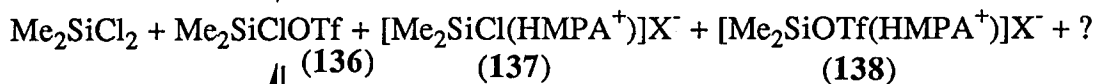
NMI ($r \leq 3$), it is obvious that a number of processes were going on, including the exchanges of leaving group and association of the nucleophile as there were either several ²⁹Si signals together with sets of proton signals or null ²⁹Si NMR signal. However there were only two ²⁹Si signals with four equivalents of NMI present, one corresponding to Me₂SiCl₂ and the other corresponding to a hexacoordinate complex (135) from MeHSiOTf₂. As a matter of fact, a solid adduct was isolated from the mixture two days later and was found to be MeHSiOTf₂·4 NMI by elemental analysis and solution NMR. The results clearly demonstrates the exchange of leaving groups between two silanes and the Si-H containing silane being much more reactive.

MeHSiCl₂ + Me₂SiOTf₂ + HMPA

The NMR spectra of the mixtures of MeHSiCl₂ and Me₂SiOTf₂ with HMPA in solution are complicated as well. However some of the intermediates involving exchanges of the leaving groups and association of the nucleophiles can be interpreted as shown in Scheme 2.21.

In the presence of small equivalents of HMPA ($r \leq 2$) there were a number of signals in the ²⁹Si NMR spectra, which indicates several dimethylsilyl intermediates formed while the H-containing moieties (MeHSi) engaged in fast exchanges. The dimethylsilyl compounds include a small amounts of a mono-substituted adduct [Me₂SiOTf(HMPA⁺)]X⁻ (**138**) (6.74 ppm) and silanes from exchanging leaving groups such as Me₂SiCl₂ (33.1 ppm) and Me₂SiClOTf (**136**) (29.4 ppm). They were in slow exchange with each other and can form a mono-substituted adduct [Me₂SiCl(HMPA⁺)]X⁻ (**137**) (17.8 ppm), which was surprisingly stable as the signals were sharp and the ²⁹Si-³¹P coupling was nicely observed. Presumably methylhydrosilyl are more reactive species but the exchanges were too fast to be recorded by ²⁹Si NMR spectrum. The proton and ³¹P NMR data support this explanation. Therefore the reactivity enhancement of dimethylsilyl species by a good leaving group is significant indeed.

In the presence of three equivalents of HMPA, there were only two signals in the ²⁹Si spectrum. The one at 16.5 ppm corresponded to **137** in fast exchange with free HMPA as there was no coupling observed. The other at -26.8 ppm, being a triplet with nearly 300 Hz coupling with ¹H, corresponded to a doubly substituted adduct [MeHSi(HMPA⁺)₂]X⁻² (**129**), which was reactive enough to associate another HMPA to produce a pentacoordinate complex (**131**) while the dimethylchlorosilane complex **137** remained little changed in the equilibria when the fourth equivalent of HMPA was added. NMR data of the protons and ³¹P were in agreement with this interpretation.



r	$\delta^{29}\text{Si}$	$J_{\text{Si-H}}$	$J_{\text{Si-P}}$	$\delta^{31}\text{P}$	$\delta^1\text{H}$ (ppm)		
	(ppm)	(Hz)	(Hz)	(ppm)	(HSi)	(MeSi)	(HMPA)
1	33.14(Me ₂ SiCl ₂)	7.8			5.35,	0.77,	
	29.35(136)	6.9			5.45	0.82,	
	17.82(d, 137)	7.8	10.8	26.4(br)	(br)	0.85,	2.84, 2.72
	6.74(s,d, 138*)	7.8	7.8			0.84	
2	33.36(s, Me ₂ SiCl ₂)	7.8		26.35	5.45	0.82	
	17.74(l,d, 137)	7.8	10.8	27.73	5.54	0.78	2.83, 2.72
				(sbr)	(sbr)		
3	16.51(137)	7.8		26.15		0.79	
	-26.77(t, 129)	298.8	4.9	(sbr)	5.48	(sbr)	2.83, 2.71
4	16.40(137)	7.8		24.9		0.79	
	-68.35(br, 131)	308.6		(sbr)	5.57	0.72	2.75, 2.62

Scheme 2.21 Competitive reactions of the mixtures of MeHSiCl₂ and

Me₂SiOTf₂ and HMPA in CD₃CN + CDCl₃ (X = Cl or OTf).

* s and l indicate the size of the signal to be at least 60% smaller or larger relative to other signals in the spectra; the size was about the same if not specified.

Similar reactions were observed by NMR with the mixtures of MeHSiCl_2 and Me_2SiBr_2 (or Me_2SiI_2) and r HMPA in mixture solvent of CD_3CN and CDCl_3 .

Summary

The reactivity of silanes R_2SiX_2 and MeHSiX_2 is controlled by both the R group and the leaving group X.

The steric hindrance of the R group and hydrogen, just as it affects the coordination chemistry, also contributes to the reactivity of difunctional silanes. The reactivity of Me_2SiX_2 and Ph_2SiX_2 towards nucleophiles are similar because their coordination chemistry is similar, though some of the intermediates of the phenylsilane are more labile. A replacement of a methyl or phenyl group by H will increase the reactivity of the silane greatly as it becomes easier to form extra coordination at silicon in addition to the maximum coordination number being increased by one. That is, the reactivity and the readiness to increase coordination of the silanes with nucleophiles have the same order: $\text{Ph}_2\text{SiX}_2, \text{Me}_2\text{SiX}_2 \ll \text{MeHSiX}_2$.

A silane that has a good leaving group, such as triflate, will have a higher reactivity than a silane with relatively poor leaving groups such as chlorine. However, the leaving groups of one silane can exchange with the leaving groups of another under catalysis of a nucleophile. In this way, the reactivity of all the silanes involved will be enhanced not necessary by the intermediates created by the catalyst but by an enhanced reactivity of the silane itself bearing a good leaving group.

2.6 Conclusion to Chapter 2

The interactions of acyclic difunctional silanes R_2SiX_2 (R = Me, Ph, H; X = Cl, Br, I, OTf) with neutral nucleophiles in solution were observed with NMR spectroscopy, together with the analysis results of some solid adducts isolate from the reaction systems, to form tetra-, penta- and hexa-coordinated silicon complexes. The

production of ionic species in the reaction processes was detected by conductivity titration studies of the mixtures in solvent. A combination of these results allows many of the silane-nucleophile adducts to be identified definitively.

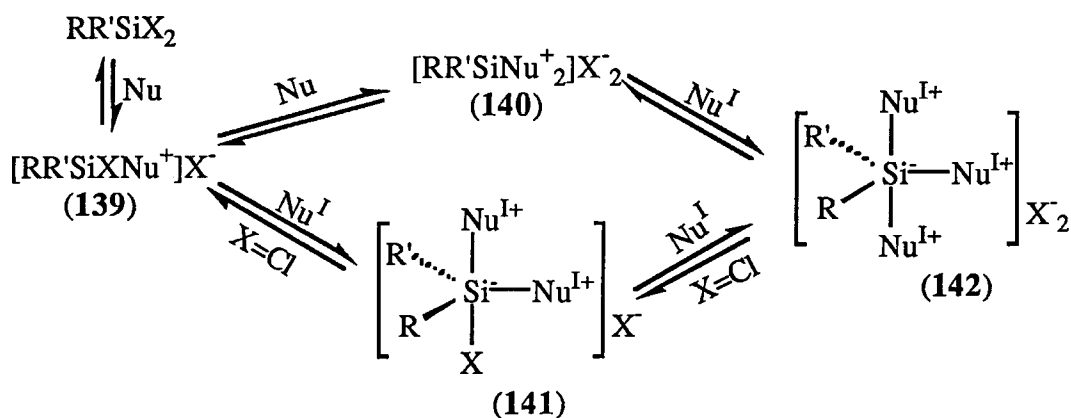
The coordination at silicon has long been the key question in interpretations of the nucleophilic reaction mechanisms of silicon compounds⁷⁸. It is fascinating that the interactions of R_2SiX_2 with nucleophiles produce complexes with coordination number from four to six, covering all those proposed but disputed coordinations of various intermediates. However the coordination at silicon is a balance between the steric and electronic effects from the substituents and the nature and quantity of the attacking nucleophiles.

Difunctional silanes have a higher tendency than mono-functional silanes to increase their coordination number at silicon with nucleophiles and ultimately form complexes with coordination number one greater than those of the corresponding mono-functional silane. This probably arises from the increased electropositivity at silicon with the increased numbers of electron withdrawing functional groups. However, the steric effect is not negligible. The reported formation of $Me_3Si(CN)_2^-$ and complex **4**^{149, 49} can be interpreted by considering the decreased steric hindrance either by the small size of CN^- or, in the case of **4**, a strained four-membered ring structure.

The significant effects of steric hindrance are more clearly reflected by the much enhanced ability of difunctional silanes to increase their coordination number at silicon in compounds in which Me or Ph has been replaced by H. Less spacially demanding nucleophiles (Nu^I = NMI, DMAP and DMF) also prefer to form complexes with higher coordination number than spacially demanding nucleophiles (Nu^{II} = HMPA and DMPU). The final adducts of difunctional silanes with Nu^I always have a coordination number increased by one than those with Nu^{II} .

Although extracoordination at silicon is common in the interaction of difunctional silanes with nucleophiles, a substitution process is not unusual. The reaction pathways of R_2SiX_2 with nucleophiles (Nu , including Nu^I and Nu^{II}) are generalised

in Scheme 2.22 for $RR'SiX_2$ ($R, R' = Me, Ph; X = Cl, Br, I, OTf$) and in Scheme 2.16 for $RHSiX_2$ ($R = Me, Ph; X = Cl, OTf$).



Scheme 2.22 The reaction mechanisms of $RR'SiX_2$ with nucleophiles.

At low equivalents of nucleophiles ($r \leq 1$), $RR'SiX_2$ produces mono-substitution tetracoordinate adducts(139), which matches Frye's results². Under similar conditions, $RHSiX_2$ prefers an association process to form pentacoordinate complexes (121 and 128) except the chlorosilane with Nu^I (122a). $RR'SiX_2$ finally results in only pentacoordination with Nu^I (142) and tetracoordination with Nu^{II} (140) while $RHSiX_2$ produces hexacoordination (126 and 127) with Nu^I and pentacoordination (131) with Nu^{II} . The maximum coordination number at silicon is not dependent on the nature of the leaving group of the silanes and the nucleophilicity of the nucleophiles but the number of leaving groups and the size of the alkyl groups (R or H) of the silane and the possible steric hindrance of the nucleophiles upon complexation.

The reaction pathways are also complicated as the coordination at silicon and the stability of the intermediates change with the nature of the R groups (Me or Ph or H), the nature of the leaving groups of the silanes and the nature of the nucleophiles. For example, the intermediates of phenyl silanes are more labile to be attacked; with two equivalents of nucleophiles the chlorosilanes prefer a mono-substituted

pentacoordinate structure (**124**, **130** and **141**) while the others form doubly substituted tetracoordinated adducts(**123**, **129** and **140**).

The reactivity of a silane is associated with the coordination chemistry of that silane. The more ready is coordination, the more reactive is the silane; that is RHSiX_2 is more reactive than RR'SiX_2 . Additionally, the leaving groups contribute to the reactivity of the silanes significantly. The reactivity of the silanes is in an order according to their leaving groups: $\text{I}^- > \text{OTf}^- > \text{Br}^- \gg \text{Cl}^-$. Therefore the exchanges of leaving groups under the catalysis of a nucleophile can possibly modify the reactivity of a silane simply by changing a leaving group.

The nucleophilicity of a nucleophile, measured by Taft's Beta values, also affects the reaction equilibrium constant K , though no evidence is found to change the reaction course. Strong nucleophiles have a larger K and weak nucleophiles have a smaller K . In fact the reactions of weak nucleophiles such as DMF and DMPU with chorosilanes are difficult to be observed at room temperature. Their reaction mechanisms illustrated in Scheme 2.22 and Scheme 2.16 are just an indication of the tendency of such weak nucleophiles and the reaction under normal condition will actually be of little significance.

Chapter 3 Interactions of nucleophiles with RSiX_3 ($\text{R} = \text{Me, Ph, H}$; $\text{X} = \text{F, Cl, OTf}$)

3.1 Introduction

It is most likely that the coordination chemistry of silicon is closely related to the numbers of electronegative groups surrounding silicon. In Chapter 2 it is shown that difunctional silanes are more ready to increase their coordination with nucleophiles than the corresponding monofunctional silanes, and that the nucleophilic reaction at silicon can take various approaches with different coordination. In this chapter similar reaction systems with trifunctional silanes RSiX_3 ($\text{R} = \text{Me, Ph, H}$; $\text{X} = \text{F, Cl, OTf}$) and nucleophiles ($\text{Nu} = \text{NMI, DMAP, DMF, HMPA and DMPU}$) in solution are to be examined by the same methods.

Trifunctional silanes are relatively easy to complex with nucleophiles. For example, Corriu¹⁵⁰ recently reported his results of mechanistic study on trifunctional pentacoordinated (aminoaryl)silanes and proposed the inversion of the TBP structures occurred by an "irregular process" corresponding to $\text{Si} \leftarrow \text{N}$ bond breaking and reclosure. However only a limited amount of information is available on the acyclic systems. Most data relate to poor leaving groups. RSiF_3 was found to

coordinate F^- forming pentacoordinated tetrafluorosilicate series $RSiF_4^-$, which underwent fast intramolecular exchange^{54, 148a}. $HSi(OR)_3$ only associated very strong nucleophiles such as HK and KOR^{130, 131}. Although $MeSiCl_3$ with HMPA was studied by ^{31}P NMR, no result on silicon was obtained¹⁴⁷. Therefore it is interesting to know the coordination chemistry and reaction pathways of acyclic simple tri-functional silanes with neutral nucleophiles.

The subsequent discussion is divided into three sub-sections, each dealing with a particular class of silanes reacting with selected neutral nucleophiles:

- (i) $MeSiX_3$ ($X = Cl, OTf$);
- (ii) $PhSiX_3$ ($X = F, Cl$);
- (iii) $HSiX_3$ ($X = Cl, OTf$).

3.2 The interaction of $MeSiX_3$ ($X = Cl, OTf$) with nucleophiles

The interactions of trifunctional silanes with nucleophiles were studied by the same methods used in Chapter 2. The nucleophiles selected are the same and are divided into two groups in the same way as well.

3.2.1 The interaction of $MeSiCl_3$ with nucleophiles

$MeSiCl_3 + NMI$

The titration of $MeSiCl_3$ with NMI against NMR properties of the solution is listed in Table 3.1. The addition of NMI into $MeSiCl_3$ in $CDCl_3$ produced solids, which dissolved by adding CD_3CN . The ^{29}Si NMR signal disappeared with up to three equivalents of NMI ($r \leq 3$) but reappeared at a high field (-176 ppm) within the range of hexacoordinate silicon with four equivalents of NMI. Further addition of NMI did not alter the position of the signal much but kept a sharp signal at about -178 ppm. Although the proton signals of the methyl group of the silane moiety had hardly changed, the protons of NMI showed that NMI complexed with $r \leq 4$ and there were

Table 3.1 NMR data of the mixtures of $\text{MeSiCl}_3 + r \text{ NMI}$

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)	
		(MeSi)	(NMI)
0.0	12.01	1.13	(7.37, 6.96, 6.85, 3.53)
1.0	Null	1.15	8.52, 7.23, 7.13, 3.88
2.0	Null	1.14	8.61, 7.20, 7.19, 3.91
3.0	Null	1.13	8.65, 7.24, 7.17, 3.93
4.0	-176.0(s,br)	1.13	8.66, 7.27, 7.21, 3.95
5.0	-177.72	1.14	8.49, 7.23, 7.03, 3.89
6.0	-177.89	1.14	8.4(br), 7.21, 7.03, 3.86
7.0	-177.97	1.14	8.3(br), 7.18, 7.02, 3.83

c = 0.34 mmol./ml related to the silane in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

exchanges between the NMIs free and associated with $r > 4$. These observations mean MeSiCl_3 formed hexacoordinated silicon with four equivalents of NMI; that is a complex $[\text{MeSi}^2\text{-Cl}(\text{NMI}^+)_4]\text{Cl}^-_2$ was produced in the equilibrium. Elemental analysis and solution NMR examination of the solids isolated in the mixture confirm the existence of such a complex with a formula of $\text{MeSiCl}_3 \cdot 4 \text{ NMI} \cdot \text{CHCl}_3$.

$\text{MeSiCl}_3 + \text{DMAP}$ (or DMF)

Similar NMR studies of the interactions of MeSiCl_3 with DMAP or DMF in solution were performed. Some of the ^{29}Si chemical shifts of the mixtures are collected in Table 3.2. The interaction of DMAP with MeSiCl_3 produced hexacoordinate

Table 3.2 $\delta^{29}\text{Si}$ values (ppm) of the mixtures of MeSiCl_3 with DMAP and DMF.

r	$\text{MeSiCl}_3 + r \text{ DMAP}$	$\text{MeSiCl}_3 + r \text{ DMF}$
3.0	-	12.49
4.0	-	Null
6.0	-149.9*	Null**
7.0	-150.56	Null

* The titration was done with addition MeSiCl_3 into DMAP in $\text{CD}_3\text{CN} + \text{CDCl}_3$ solution;

Solids precipitated as with more silane added. $c = 0.2 \text{ mmol./ml}$ related to DMAP.

** Still null signal at 223 K; $c = 0.6 \text{ mmol./ml}$ related to the silane in CDCl_3 .

complexes as the sharp signal at about -150 ppm was in the range of hexacoordinate silicon. A solid separated from the interaction solution was found by elemental analysis and NMR examination to have the formula of $\text{MeSiCl}_3 \cdot 4 \text{ DMAP} \cdot \text{CDCl}_3$, which is similar to that of NMI. The interaction of DMF with MeSiCl_3 was weak at low concentration ($r \leq 3$) as the ^{29}Si NMR signal had hardly changed. However with more than four equivalents of DMF, the interaction was impossible to observe with ^{29}Si NMR as there was no signal.

Conductivity studies of MeSiCl_3 with NMI (or DMAP or DMF)

Conductivity studies of the titrations of MeSiCl_3 and NMI, DMAP or DMF have shown ionic species to be produced in all these mixtures as illustrated in Figure 3.1. The immediate increase of conductivity of the solution upon addition of NMI to MeSiCl_3 indicates ions formed with small amount of NMI. The decreasing conductivity when NMI was between 0.5 and 1.1 equivalents suggests the ions formed were partially neutralized internally, which may correspond to further

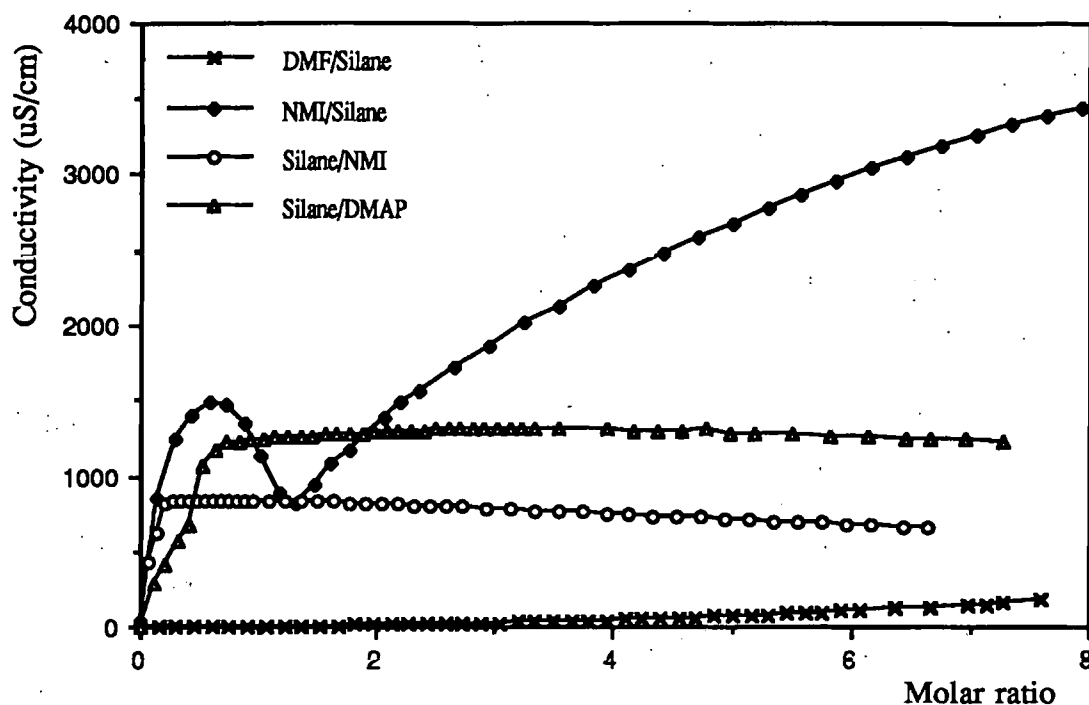


Figure 3.1 Conductivity titrations of MeSiCl_3 and nucleophiles.

The concentrations were 0.25, 0.14, 0.21 and 0.14 mmol./ml related to the titrates respectively to DMF/Silane, NMI/Silane, Silane/NMI and Silane/DMAP in $\text{CD}_3\text{CN} + \text{CDCl}_3$ except DMF/Silane, which was done in CDCl_3 .

complexation of the produced ions. The continued increases of conductivity when NMI was more than 1.1 equivalents show ionic species resulted in the reaction.

Summary

By combination of the results of NMR and conductivity studies of the interactions of MeSiCl_3 with NMI, (including perhaps DMAP and DMF), a reaction pathway can be rationalized as shown in Scheme 3.1. Although null ^{29}Si NMR signal was observed with small amounts of NMI ($r < 4$), **143** can be rationalized to be responsible for the initial increases of conductivity and **144** for the followed decreases if the ions are not tightly paired. Further substitutions, probably by way of **145** and **146**, lead to increases of conductivity again and finally result in hexacoordinate complexes **147**. There is no evidence for the last remaining Si-Cl bond being replaced.



The interactions of MeSiCl₃ with spacially demanding nucleophiles, such as HMPA and DMPU, proved to be different by NMR studies. Some of the ²⁹Si NMR data are collected in Table 3.3.

There is hardly any reaction observed by NMR with the mixtures of MeSiCl_3 and DMPU as the ^{29}Si NMR signal remained unchanged even with high proportion of DMPU and at low temperature, though an exothermic phenomenon was noted when the first equivalent of DMPU was added to MeSiCl_3 solution.

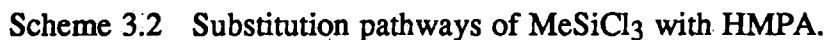
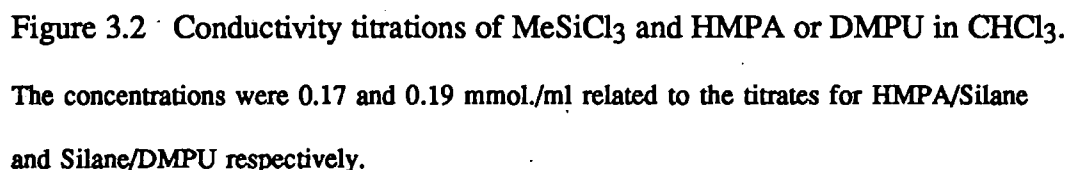
Table 3.3 ^{29}Si chemical shifts of the mixtures of $\text{MeSiCl}_3 + r$ HMPA
(or DMPU) in CDCl_3 .

r	$\text{MeSiCl}_3 + r$ HMPA (c = 0.6 mmol./ml)	$\text{MeSiCl}_3 + r$ DMPU (c = 0.3 mmol./ml)
1.0	10.31	12.29
2.0	4.66	12.51
3.0	-0.27(sbr)	12.62
4.0	-6.69(sbr)	12.78
5.0	-16.02(br)	12.84
6.0	-36.2(vbr)	12.85
6.0 (at 223 K)	-74.26(br)	11.94

Conductivity studies of $\text{MeSiCl}_3 + \text{HMPA}$ (or DMPU)

Conductivity studies of the interactions of MeSiCl_3 with HMPA or DMPU also showed that ionic species produced with MeSiCl_3 and HMPA while there is no significant reaction between MeSiCl_3 and DMPU as illustrated in Figure 3.2.

However, the concentration of the ions produced was very low when HMPA was less than 2.2 equivalents. The conductivity of the mixture only started to increase with significance when more than 2.2 equivalents of HMPA was present. Therefore it is more likely that the substitution of the chlorine atoms was performed within pentacoordinated species as shown in Scheme 3.2. By fast exchanges of MeSiCl_3 with **148**, the chemical shift of silicon-29 can move to higher field while the



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3.2.2 The interaction of MeSiOTf₃ with nucleophiles

The replacement of chlorine by triflate group of the methyl trifunctional silane not only made its reaction with nucleophiles more exothermic but also produced a greater tendency to increase the coordination at silicon, though the highest coordination numbers at silicon of the most stable silane-nucleophile complexes were not changed.

MeSiOTf₃ + NMI

The interaction of MeSiOTf₃ with NMI in solution monitored by ²⁹Si and ¹H NMR showed that hexacoordination of silicon is dominant in the complexes as illustrated in Table 3.4. The ²⁹Si chemical shift for hexacoordinated adducts appeared (-163.8 ppm) together with a value of the unreacted silane in equilibrium (-59.3 ppm) with only one equivalent of NMI present. This means two equivalents of NMI directly associated with silicon forming hexacoordination [MeSi²⁺-OTf₃(NMI⁺)₂] without substitution, probably by an activated pentacoordinated intermediate [MeSi-OTf₃(NMI⁺)] (which was not observed by ²⁹Si NMR but was possibly indicated by the two sets of proton signals where 0.5 and one equivalents of NMI were present). The first substitution of the triflate group was performed within the six-coordinated complexes as clearly showed by the switch of the ²⁹Si chemical shift from about -167 ppm to -170 ppm together with the alternation of proton signals when NMI was increased from 1.5 to 3 equivalents, though that means the exchange between [MeSi²⁺-OTf₃(NMI⁺)₂] and [MeSi²⁺-OTf₂(NMI⁺)₃]OTf⁻ was quite slow on the NMR time scale. However, the second substitution is not so certain as null ²⁹Si signal was recorded when NMI was increased to four equivalents. Nonetheless solid adducts were easy to deposit at this point. The solids isolated have a formula of MeSiOTf₃-4 NMI, probably corresponding to a doubly substituted complex [MeSi²⁺-OTf(NMI⁺)₄]OTf⁻₂. The sharp resonance signal of silicon-29 at -177.5 ppm corresponds to a triple-substituted hexacoordinated species [MeSi²⁺-(NMI⁺)₅]OTf⁻₃ as the signal remained unchanged with further addition of NMI, though the associated

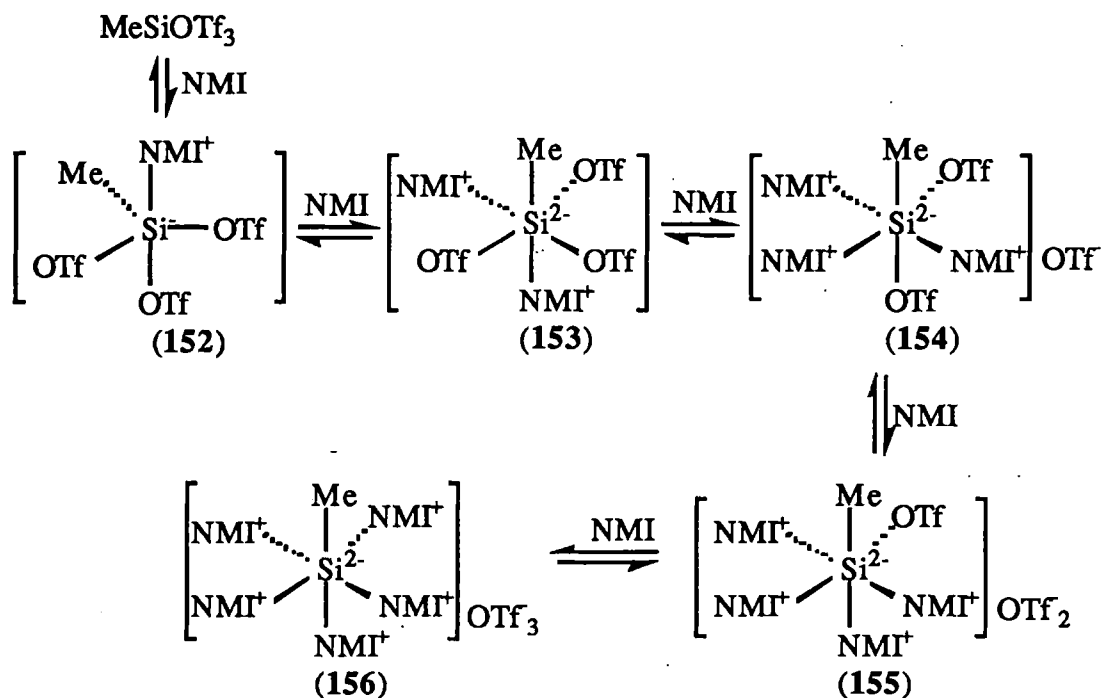
Table 3.4 NMR data of the mixtures of MeSiOTf₃ + r NMI in CD₃CN + CDCl₃.

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}(\text{ppm})$	
		(MeSi)	(NMI)
0.0	-55.48	1.21	(7.37, 6.96, 6.85, 3.53)
0.5	-57.93(sbr) Null	1.20(l)* 0.91, 0.86	8.50, 8.38; 7.56, 7.29, 7.06; 3.95, 3.84
1.0	-59.27(s,sbr) -163.82(sbr)	1.20(s) 0.91, 0.86	8.49, 8.38; 7.56, 7.27, 7.01; 3.94, 3.83
1.5	-165.63(sh) -171.39(s)	0.91 1.10(s)	8.33, 7.46, 7.09, 3.83 8.48, 7.57, 7.26, 3.89(all s)
2.0	-166.94 -170.80(s)	0.90 1.05(s)	8.31, 7.46, 7.10, 3.83 8.45, 7.53, 7.21, 3.86(all s)
2.5	-167.36 -170.24	0.90 1.05	8.30, 8.11, 7.43(sbr), 7.12(br), 3.82, 3.83
3.0	-169.41(sh)	1.04	8.22, 7.42, 7.09, 3.83
4	Null	1.00	8.22, 7.23, 6.96, 3.84
5	-177.47(sh)	0.99	8.08, 7.22, 6.90, 3.82
6	-177.48	1.00	8.06, 7.20, 6.87, 3.82
8	-177.56	0.99	7.89, 7.11, 6.97, 3.74

* l and s indicate the size of the signal. l, means a large one with at least 60% larger than the others; s, means small and is less than 20% of the others; If not indicated, the size is about the same or normal line shape.

c = 0.3 mmol./ml related to the silane.

NMI could exchange with those free NMI. Therefore the interaction of MeSiOTf₃ with NMI presents a very good example for substitutions at hexacoordinated silicon, as shown in Scheme 3.3.



Scheme 3.3 Nucleophilic substitution of MeSiOTf₃ with NMI.

MeSiOTf₃ + DMF

The enhanced reactivity caused by the better leaving group OTf is also reflected by the interaction of MeSiOTf₃ with the weak nucleophile DMF. Some of the NMR data of the mixtures are shown in Table 3.5. Although null signal of any adducts was recorded in the ²⁹Si NMR spectra with one to three equivalents of DMF, the significant increases of shielding of the protons of the MeSi moiety and the deshielding of the protons of DMF indicate there were associated species undergoing intermediate exchange. The ²⁹Si resonance signal at high field (-164.56 ppm) with four equivalents of DMF, remained with more DMF added, suggesting a hexacoordinated complex was produced. This complex is quite stable and the DMFs

Table 3.5 NMR data of the mixtures of MeSiOTf₃ + r DMF.

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)	
		(MeSi)	(DMF)
1.0	-57.79(s,br); Null	0.9(vbr)	8.19, 3.38, 3.27
2.0	Null	0.62(br)	8.17, 3.34, 3.21
3.0	Null	0.49(sbr)	8.20, 3.35, 3.20
4.0	-162.4(s,br)	0.36	8.22, 3.34, 3.16
5.0	-164.56(sh)	0.29	8.21, 3.31, 3.12
7.0	-164.56	0.29	8.17, 3.16, 3.02(all br)

c = 0.4 mmol./ml related to the silane in CD₃CN + CDCl₃.

can exchange between those free and associated as the $\delta^{29}\text{Si}$ value kept constant while the proton signals of DMF became more and more broadened and deshielded, though it is not certain to what degree the triflate groups were substituted.

MeSiOTf₃ + DMAP

The titration of DMAP with MeSiOTf₃ in CD₃CN + CDCl₃ while monitoring NMR properties was carried out in the usual way but only one ²⁹Si resonance signal at -111.20 ppm ($\delta^1\text{H}_{(\text{MeSi})} = 1.07 \text{ ppm}$) with strong intensity was observed with one equivalent DMAP, which indicates the formation of a pentacoordinate complex, most likely [MeSiOTf₃(DMAP⁺)]. The signal disappeared with increases of the equivalents of DMAP up to six. Presumably the hexacoordinated complexes formed afterwards were exchanging as indicated by a very broadened proton signal at about 0.8 ppm of the MeSi moiety.

Conductivity studies of MeSiOTf₃ + NMI (or DMF or DMAP)

The conductivity titration studies of the interaction of MeSiOTf₃ with NMI and DMAP were not so successful, as solids were produced even in the solvent mixture of CH₃CN and CHCl₃. However, both showed significant conductivity increases when the nucleophile was present at ratios of more than two. The titration of MeSiOTf₃ with DMF displayed a similar tendency as shown in Figure 3.3. Although the

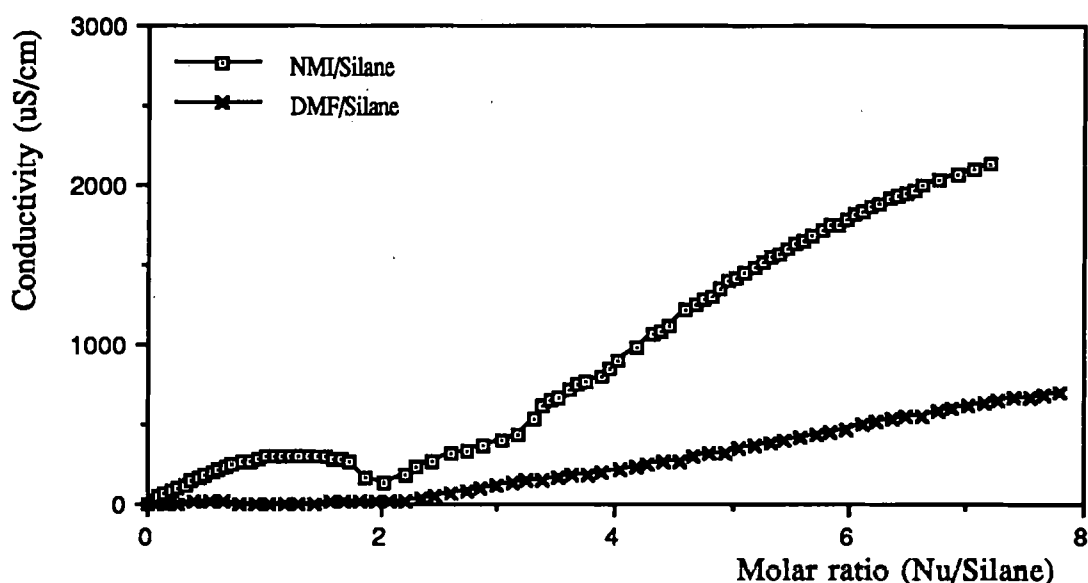


Figure 3.3 Conductivity titrations of MeSiOTf₃ with NMI or DMF.

* $c = 0.15$ mmol./ml related to MeSiOTf₃. The titration with NMI in CD₃CN + CDCl₃ produced solids between 1.8 and 5.0 equivalents of NMI. The titration of DMF was done in CDCl₃.

existence of solids affected the readings of conductivity in the titration of MeSiOTf₃ with NMI, a general trend can still be observed. The initial small increases of conductivity can be attributed to a small amount of mono-substituted tetracoordinate adducts in equilibrium with **152** and, more likely, a small amount of **154**. The large increases of conductivity starting from two equivalents of NMI corresponding to the progressive substitution process. DMF titrating against MeSiOTf₃ presents a very similar conductive property, though the magnitude of the conductivity reading was

much smaller because it was in CHCl_3 and the triflate groups were not totally substituted in the reaction. Therefore the conductivity measurements of the mixtures of MeSiOTf_3 with NMI or DMF are in general agreement with the results from NMR studies, as presented in Scheme 3.3.

$\text{MeSiOTf}_3 + \text{HMPA}$

In contrast with the overwhelming formation of hexacoordination of nucleophiles Nu^{I} (NMI, DMAP and DMF) with MeSiOTf_3 , NMR examinations of the interactions of spacially demanding nucleophiles Nu^{II} (HMPA and DMPU) with MeSiOTf_3 showed that they can only reach pentacoordination, though solids were always produced with more than three equivalents of HMPA present.

The NMR data of the mixtures of MeSiOTf_3 with HMPA, see Table 3.6, suggest the first equivalent of HMPA was directly associated to silicon to form a pentacoordinate

Table 3.6 NMR data of the mixtures of $\text{MeSiOTf}_3 + r \text{ HMPA}$.

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^{31}\text{P}$ (ppm)	$\delta^1\text{H}$ (ppm)	
			(MeSi)	(HMPA)
0.9	-98.53(d)*	26.62	1.15	2.86, 2.74
1.8	-69.84(s,sh), -74.39(sh)	27.66	1.24	2.86, 2.74(s) 2.90, 2.77
2.7	-69.81(sh) -74.99(sh)	27.60	1.23	2.87, 2.77(br)
3.0**	-69.81(sh)	27.76	1.21	2.90, 2.78

* $J_{\text{Si-P}} = 2.9 \text{ Hz}$.

** Solids produced with further addition of HMPA, though the concentration was 0.1 mmol./ml in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

complex $[\text{MeSi}^-\text{OTf}_3(\text{HMPA}^+)]$ for the ^{29}Si resonance not only shifted to a high field within the range of pentacoordinate silicon but also split into a doublet due to the coupling of ^{29}Si with ^{31}P . However, the next step upon further addition of HMPA is not certain because the chemical shifts of silicon-29 were in the range between tetra- and penta-coordinate silicon and the NMR properties of ^{31}P and ^1H did not supply much information on the coordination. It looks like a slow exchange and substitution process within tetracoordinate complexes as the $\delta^{29}\text{Si}$ values switched from -74 ppm to -69.8 ppm as the equivalents of HMPA changed from 1.8 to three. However, it is more reasonable to interpret the signal at -74 ppm to be the result of a very fast exchange between a pentacoordinate complex $[\text{MeSi}^-\text{OTf}_2(\text{HMPA}^+)_2]\text{OTf}^-$ and a tetracoordinate adduct $[\text{MeSi}^-\text{OTf}(\text{HMPA}^+)_2]\text{OTf}^-$. In this way the simple substitution of OTf with HMPA will not shift the chemical shift of silicon-29 to low field as demonstrated in Table 3.6.

MeSiOTf₃ + DMPU

Examination of the interaction of MeSiOTf₃ with DMPU by ^{29}Si and ^1H NMR presents a more clear picture about the coordination and substitution at silicon. Some of the typical chemical shifts of the mixtures are collected in Table 3.7.

All the ^{29}Si NMR signals are sharp ones, which suggests quite fast exchanges in the equilibria. The first equivalent of DMPU was associated to silicon forming a neutral pentacoordinate complex $[\text{MeSi}^-\text{OTf}_3(\text{DMPU}^+)]$ as the ^{29}Si resonance signal shifted more than 50 ppm high field to -110.06 ppm, which indicated a five-coordinate silicon. The second equivalent of DMPU, judged by the shielded chemical shifts of the proton of DMPU, was also associated while the sharp ^{29}Si NMR signal remained hardly changed. This observation suggests that a substitution of a triflate group by DMPU must have taken place within the pentacoordinated species; that is a new pentacoordinate complex $[\text{MeSi}^-\text{OTf}_2(\text{DMPU}^+)_2]\text{OTf}^-$ formed. However, with the addition of the third equivalent of DMPU the pentacoordination collapsed to tetracoordination, probably with a total substitution of the triflate groups to form triple

Table 3.7 NMR data for the mixtures of MeSiOTf₃ + r DMPU.

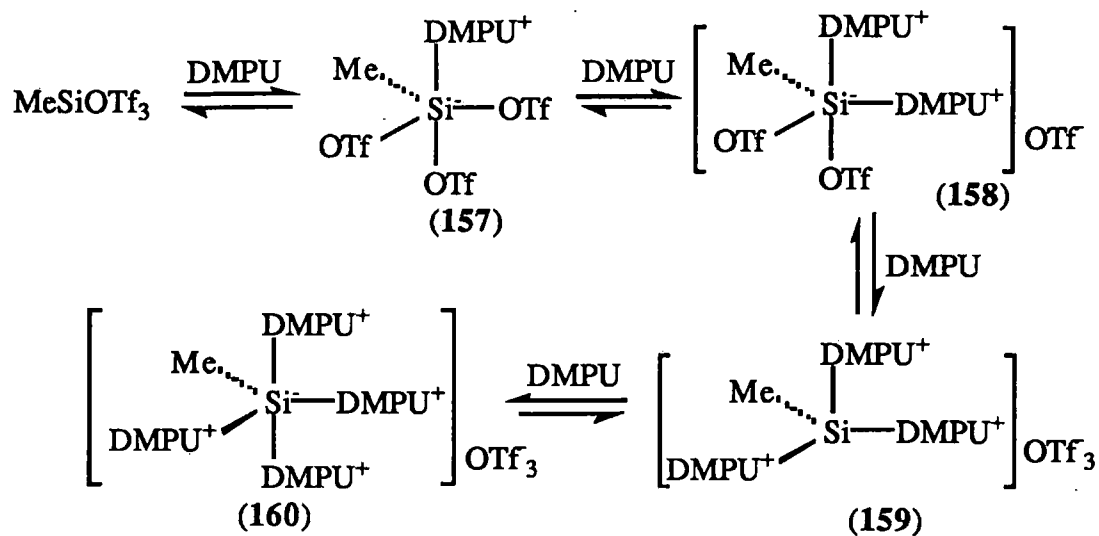
r	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)	
		(MeSi)	(DMPU)
1.0	-110.06	1.07	3.55, 3.19, 2.17(sbr)
2.0	-110.31	1.08	3.58, 3.22, 2.13(sbr)
3.0	-68.41	1.32	3.57, 3.15, 2.14(sbr)
4.0	-72.61	1.27	3.50, 3.09, 2.11(sbr)
5.0	-78.12	1.21	3.45(t), 3.05, 2.07(sbr)
7.0	-88.41	1.11	3.39(t), 2.99, 2.03(qu)
9.0	-94.92	1.05	3.36(t), 2.96, 2.01(qu)
11.0	-98.62	1.01	3.34(t), 2.94, 2.00(qu)

c = 0.6 mmol./ml related to the silane in CD₃CN + CDCl₃.

substituted tetracoordinated adduct [MeSi(DMPU⁺)₃]OTf⁻₃, indicated by the sudden drop of the chemical shift of the ²⁹Si from -110.3 ppm to -68.4 ppm, together with the pronounced deshielding of the protons of the MeSi moiety. Further addition of DMPU up to eleven equivalents just moved the ²⁹Si NMR signal smoothly to a high field of five-coordinated silicon and the protons became progressively deshielded, which indicated formation of pentacoordinate complex [MeSi⁻(DMPU⁺)₄]OTf⁻₃ in the equilibrium. No evidence of hexacoordination was found. The whole process can be expressed in Scheme 3.4.

Conductivity studies of MeSiOTf₃ + HMPA (or DMPU)

Conductivity titrations of the interactions of MeSiOTf₃ with HMPA or DMPU were successfully carried out in CHCl₃ without formation of solids, as illustrated in Figure



Scheme 3.4 Substitution pathways of MeSiOTf₃ with DMPU.

3.4. The titration curves are very similar. Both have small conductivity increases with low equivalents of nucleophiles and have pronounced increases with high equivalents of nucleophile with a common point of inflexion at about three equivalents of the nucleophile. This means they probably have a similar reaction pathway.

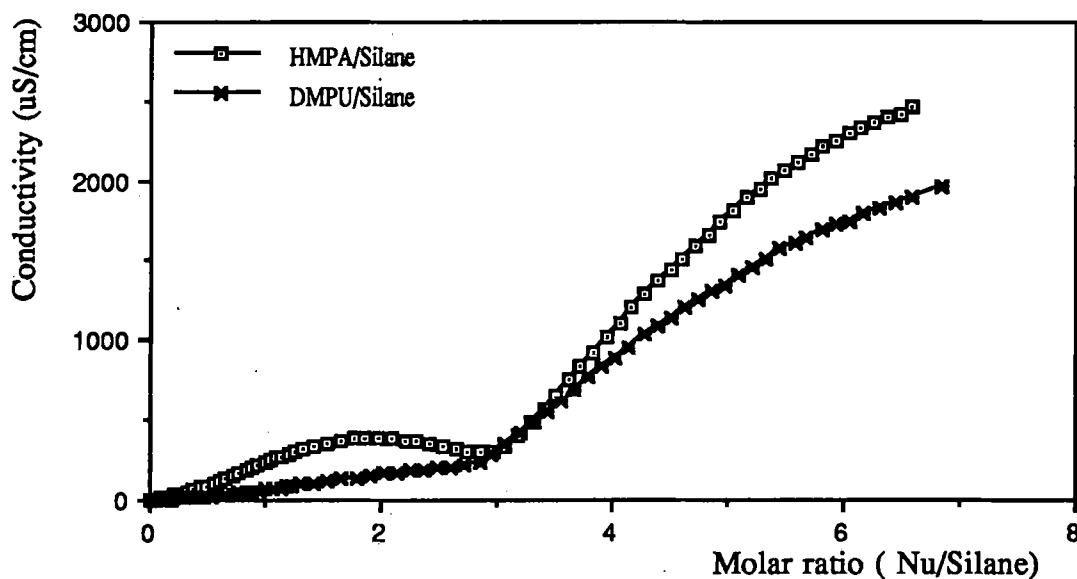


Figure 3.4 Conductivity titrations of MeSiOTf₃ with HMPA or DMPU.

$c = 0.08$ and 0.12 mmol./ml related to the silane respective to the titrations of HMPA/Silane and DMPU/Silane in CHCl_3 .

According to Scheme 3.4, ions are produced right after one equivalent nucleophile been added. However the corresponding conductivity readings were very limited until more than three equivalents of nucleophile were injected. This is probably because of the small dielectric constant of the solvent CHCl_3 . The reason the conductivity increases significantly after three equivalents of nucleophile is not that ions are produced in large quantity then but that the presence of free nucleophiles, which did not exist until the triflate group had been totally displaced, improved the dielectric constant of the solvent and thus released the ions to show their conductivity. Therefore the results of conductivity studies match the observations made by NMR of the interactions of MeSiOTf_3 with HMPA or DMPU.

3.2.3 Summary

The examinations of the interactions of MeSiX_3 ($\text{X} = \text{Cl}$ and OTf) by solution NMR and conductivity studies have shown that the coordination chemistry and the nucleophilic reaction mechanisms of trifunctional silanes are related to the nature of nucleophiles and its quantity and the nature of the leaving groups.

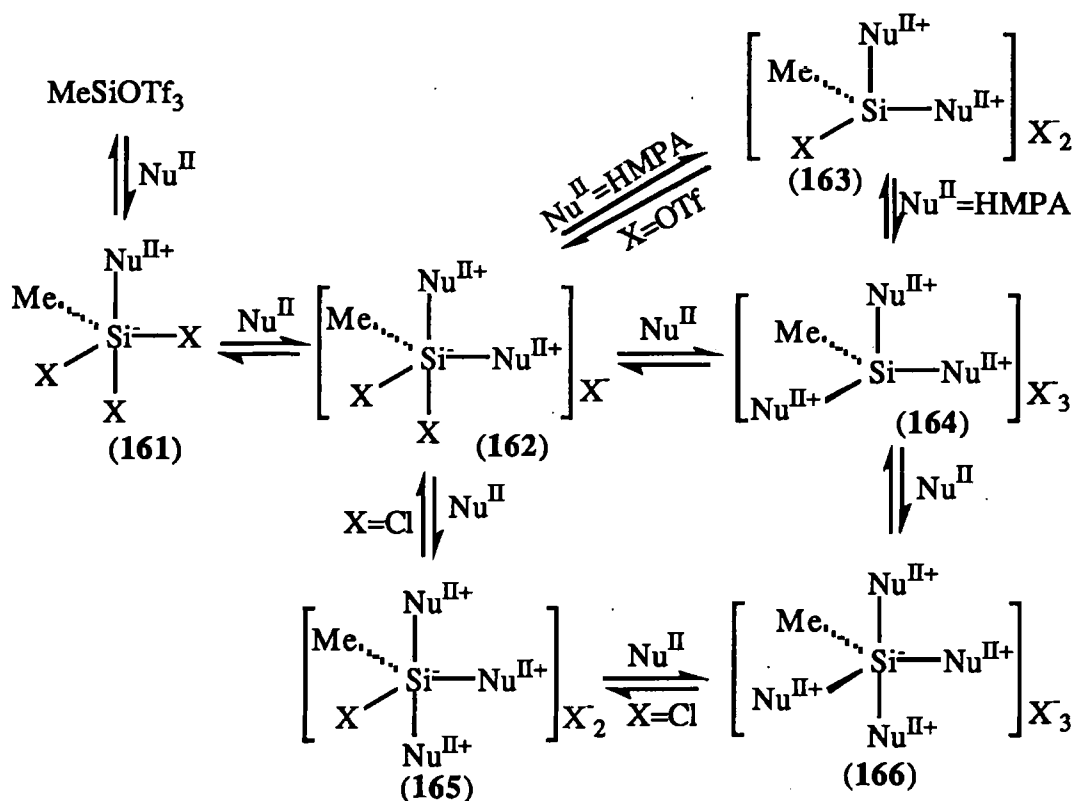
The nucleophiles

The effects of nucleophiles are determined by their steric hindrance upon complexation and by their nucleophilicities. The steric hindrance of the nucleophiles decides the coordination at silicon and the nucleophilicity affects the equilibrium constant K . The higher the nucleophilicity, measured by Taft's Beta values, the larger is K . The K can be so small that the reactions of MeSiCl_3 with weak nucleophiles such as DMF and DMPU could hardly be observed at room temperature.

The nucleophiles examined fall into two groups according to the maximum coordination number at the silicon they can induce. The first category, Nu^{I} , with smaller steric hindrance, including NMI, DMAP and DMF, finally forms hexacoordinate complexes with MeSiX_3 . The likely reaction pathways of this group of

nucleophiles with MeSiCl_3 and MeSiOTf_3 are presented in Scheme 3.1 and Scheme 3.3. Among them hexacoordinations are favourable especially with triflates, though there is a possible tetracoordinated species **143** for the chloride at the beginning of the sequence and pentacoordination in **144**, **145** and **152** is postulated at lower equivalents of nucleophiles.

The other group, Nu^{II} , includes the spacially demanding nucleophiles HMPA and DMPU, ultimately produces only pentacoordination. The reaction pathways of these nucleophiles with MeSiCl_3 and MeSiOTf_3 can be summarized by Scheme 3.5,



Scheme 3.5 The reaction pathways of MeSiX_3 ($\text{X} = \text{Cl}, \text{OTf}$) with Nu^{II} .

in which the dominant species are pentacoordinate, such as **161**, **162**, **165** and **166**, though tetracoordination with the triflate silane has been identified with **163** for HMPA and **164** for both HMPA and DMPU. No evidence of hexacoordination is found at all.

The leaving group

The contribution of the leaving groups towards nucleophilic reactions at silicon comes from their electronic properties and the leaving ability. A silane having better leaving groups such as OTf is more reactive towards the same nucleophiles, especially those weak ones, than that with relatively poorer leaving groups such as Cl. However, the maximum coordination number of a silane-nucleophile complex is not decided by the nature but the number of the leaving groups, though the coordination of the intermediates is affected.

The coordination of the intermediates is a balance between the leaving ability and the electronic properties besides the steric hindrance. On the one hand, the triflate group OTf tends to encourage high coordination such as **152**, **153**, **154**, **155**, **161** and **162** as strongly electronegative groups are able to stabilize the charges accumulated on silicon. On the other hand, there are tetracoordinate derivatives of triflates such as **163** and **164** as a good leaving group always tends to break away. It is similar for the chlorides. As a less electronegative group it produces low coordination complexes such as **143** and **145**; as a poorer leaving group there are complexes in which the Si-Cl bonds are maintained in extracoordinated complexes such as **144**, **146**, **147**, **161**, **162** and **165**. Therefore the nucleophilic substitution is a very complicated process.

3.3 The interaction of PhSiX₃ (X = Cl, F) with nucleophiles

It has been shown in Chapter two that a replacement of a methyl group by a phenyl group will lead the intermediates of the nucleophilic reactions of the difunctional silanes to be more labile without changing the coordination type of the ultimate silane-nucleophile complexes. In this section the effects of replacement of the methyl by the phenyl group of the trifunctional silane on nucleophilic reaction are examined.

3.3.1 The interaction of PhSiCl₃ with nucleophiles

PhSiCl₃ + NMI

The interaction of PhSiCl₃ with NMI was examined by ²⁹Si NMR and was very similar to that of MeSiCl₃, as shown in Table 3.8. The addition of NMI into PhSiCl₃

Table 3.8 The NMR data for the mixtures of PhSiCl₃ + r NMI.

r	δ ²⁹ Si(ppm)	δ ¹ H(ppm)*
0	-0.88	7.74, 7.50; (7.37, 6.96, 6.85, 3.53)
1.0	Null	7.59, 7.40; 8.42, 7.25, 7.12, 3.90
2.0	Null	7.25(br), 8.41, 3.92
3.0	Null	7.23(br), 8.37, 3.91
4.0	-174.84(sbr)	7.22, 7.06(both br), 8.33, 3.88
5.0	-175.00(sh)	7.17, 6.98(both br), 8.25, 3.80

* The proton signals of the phenyl group and NMI were overlapped in most cases;

The concentration of the silane was 0.6 mmol./ml in CDCl₃.

solution caused a null signal until four equivalents of NMI was present. The resonance at a high field of -175 ppm indicated the formation of hexacoordinate silicon complexes, though the proton signals of the phenyl group did not supply much information as they were overlapping with those of NMI. However the ²⁹Si signals are good enough to demonstrate the resemblance of the reactions of MeSiCl₃ and PhSiCl₃ with NMI.

A solid adduct isolated from the reaction mixture in CH₂Cl₂ was analyzed by

elemental analysis and solution NMR examination and also proved to have four equivalents of NMI combined to the silane; that is $\text{PhSiCl}_3 \cdot 4 \text{ NMI} \cdot \text{CH}_2\text{Cl}_2$

$\text{PhSiCl}_3 + \text{DMAP (DMF)}$

The interactions of PhSiCl_3 with DMAP or DMF examined in solution by NMR are also more or less the same as those of MeSiCl_3 . Some typical chemical shifts of silicon-29 of the interaction solutions are listed in Table 3.9. The mixture of PhSiCl_3

Table 3.9 The $\delta^{29}\text{Si}$ values of the mixtures of PhSiCl_3 with DMAP and DMF.

r	$\text{PhSiCl}_3 + r \text{ DMAP}$ (c=0.3 mmol./ml in $\text{CD}_3\text{CN} + \text{CDCl}_3$)	$\text{PhSiCl}_3 + r \text{ DMF}$ (c=0.6 mmol./ml in CDCl_3)
6.0	-152.22(sh)	-
7.0	solids produced	-0.95(sbr)
7.0 (223K)	-	-176.25(sh)

with six equivalents of DMAP produced a sharp ^{29}Si resonance signal at -152.2 ppm, which indicates the formation of a hexacoordination complex. Although the mixture of PhSiCl_3 with seven equivalents of DMF had a barely changed ^{29}Si NMR signal from that of PhSiCl_3 at room temperature, there was a sharp signal with a high field ^{29}Si NMR chemical shift of -176.25 ppm at 223 K. This means that at low temperature DMF also formed a hexacoordinate species, which indicates the phenyl group is more capable of balancing the charges on silicon to produce stable extracoordination. A null ^{29}Si NMR signal was recorded with the corresponding methyl silane.

Therefore hexacoordination was observed in all the interactions of PhSiCl_3 with NMI, DMAP and DMF.

Conductivity studies of PhSiCl_3 + NMI (or DMF)

Titration of PhSiCl_3 with NMI or DMF followed by conductivity measurements of the mixtures produced nearly the same conductivity curves against the molar ratios of the nucleophile to silane as those obtained with MeSiCl_3 under similar conditions, as shown in Figure 3.1 and Figure 3.5. For the titrations with NMI, both conductivity

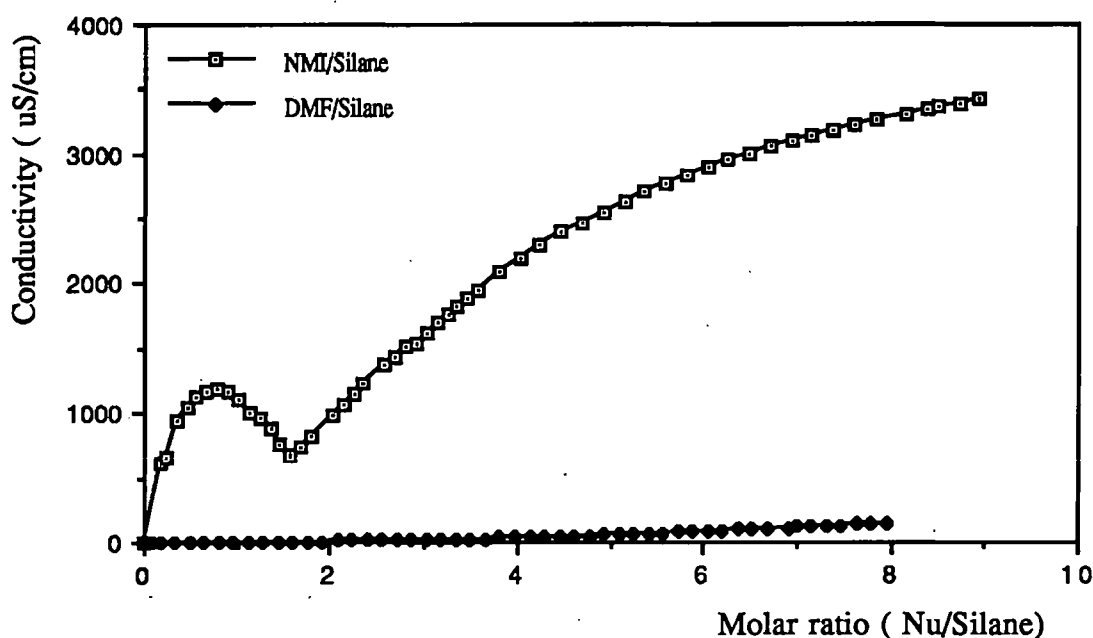


Figure 3.5 Conductivity titrations of PhSiCl_3 with NMI or DMF.

$c = 0.5 \text{ mmol./ml}$ related to the silane for the titration with NMI in $\text{CH}_3\text{CN} + \text{CHCl}_3$;

$c = 0.8 \text{ mmol./ml}$ related to the silane for the titration with DMF in CHCl_3 .

readings increased initially followed by a decrease and then increase again as the amount of NMI increased. The magnitude of the conductivity and the points of inflexion were in similar ranges to those of MeSiCl_3 . The titration with DMF was no different to that of MeSiCl_3 with DMF. Therefore the interactions of PhSiCl_3 with NMI, DMF and DMAP, probably follow the same pathway as that of MeSiCl_3 under

similar conditions as presented in Scheme 3.1.

PhSiCl₃ + HMPA (or DMPU)

The results of the NMR examinations of the interactions of PhSiCl₃ with HMPA or DMPU in solution were again similar to those of MeSiCl₃. Take the mixtures of PhSiCl₃ and HMPA for an example, see Table 3.10. The chemical shifts of the signals

Table 3.10 NMR data of the mixtures of PhSiCl₃ + r HMPA in CDCl₃.

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^{31}\text{P}$ (ppm)	$\delta^1\text{H}$ (ppm)	
			(PhSi)	(HMPA)
1.3	-8.40(sbr)	25.88(sbr)	7.75, 7.57	2.74, 2.63
2.6	-22.47(br)	25.21(sbr)	7.73, 7.55	2.73, 2.62
6.6	-55.73(vbr)	24.16(br)	7.69, 7.51	2.67, 2.61
6.6 (223 K)	-97.96(sbr))	22.38(br)	7.67, 7.46	2.63(vbr)

c = 0.6 mmol./ml related to the silane.

in the silicon-29 NMR spectra shifted progressively to high field with diminishing and broadening signal with increases in the amount of HMPA. It reached nearly -98 ppm with 6.6 equivalents of HMPA at 223 K. This means only pentacoordinate silicon species were produced, which is quite similar to that of MeSiCl₃. The NMR properties of the protons and ³¹P of the mixtures were consistent with such a rationalization. For DMPU, there is hardly any significant reaction observed with PhSiCl₃ as the ²⁹Si resonance signal only shifted to high field by 1.5 ppm even with nine equivalents of DMPU and at 230 K while the $\delta^1\text{H}$ values remained almost constant. Therefore there is not much difference between MeSiCl₃ and PhSiCl₃ in

reacting with HMPA or DMPU as far as coordination chemistry is concerned.

Conductivity studies of PhSiCl_3 + HMPA (or DMPU)

Conductivity titrations of PhSiCl_3 with HMPA or DMPU in CHCl_3 also showed the similarity of PhSiCl_3 and MeSiCl_3 as illustrated in Figure 3.2 and Figure 3.6. The

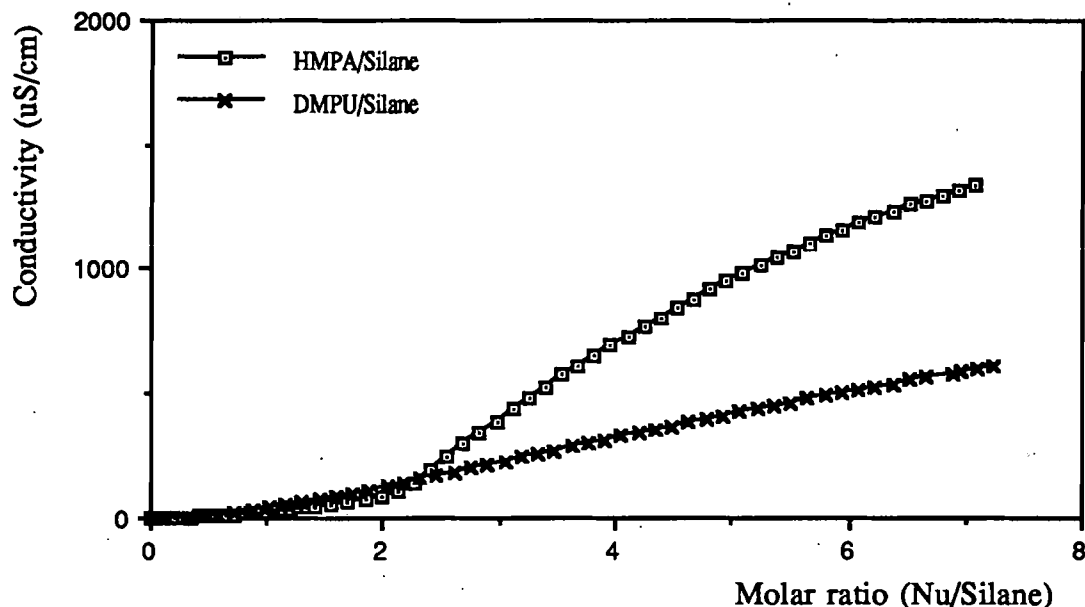


Figure 3.6 Conductivity titrations of PhSiCl_3 with HMPA or DMPU.

The concentrations were 0.5 mmol./ml related to the silane for both titrations in CHCl_3 .

conductivity curves against molar ratio of HMPA to silane are almost the same, both in shape and magnitude. Although the conductivity readings of the titration of PhSiCl_3 with DMPU were greater at high equivalents of the nucleophile, they were still small and might have a contribution from very small amounts of ionic adducts.

Summary

The results of the NMR and conductivity studies of the interaction of PhSiCl_3 with HMPA or DMPU were quite similar to those of MeSiCl_3 . The reaction mechanism and the coordination chemistry concerned can still be expressed by the one presented for the interaction of MeSiCl_3 with HMPA in Scheme 3.2, though phenyl silane may

be a little bit more reactive and the reaction with DMPU has a very small equilibrium constant K.

3.3.2 The interaction of PhSiF_3 with nucleophiles

NMR study of the interactions of fluorine silanes with nucleophiles has additional advantages over other methods as the chemical shifts of fluorines and the coupling of the ^{29}Si with ^{19}F provide invaluable information on the coordination at silicon and the position of Si-F bonds^{35, 82, 148}.

$\text{PhSiF}_3 + \text{NMI}$

Fluorine is a poorer leaving group than chlorine and triflate but is more electronegative. The interactions of PhSiF_3 with NMI as examined by ^{29}Si , ^{19}F and ^1H NMR showed the reaction took a different approach but did not change the coordination number at silicon of the final complex from those of other trifunctional silanes. Some of the typical NMR data are collected in Table 3.11.

In the ^{29}Si NMR spectra, the resonance shifted to high field progressively with the increases of the equivalents of NMI from 0.5 to four with diminished and very much broadened signals. The signals were so broadened that the coupling of ^{29}Si with ^{19}F was hardly observed. However the high field shift to -172 ppm indicates the formation of hexacoordination at silicon. With high numbers of equivalents of NMI ($r \geq 6$), especially at low temperature (220 K), a quartet span from -162.01 to -197.98 ppm with a ^{29}Si - ^{19}F coupling constant of 212 Hz was recorded. This means none of the three Si-F bonds was substituted within the hexacoordinated complex. The failure to observe the couplings with low equivalents of NMI ($r < 6$) is most likely due to the fast intermolecular exchanges between the silane-NMI complexes and the free NMI and the intramolecular movements including pseudorotations of pentacoordination and switches of bond positions within hexacoordination. Therefore the interaction of PhSiF_3 with NMI is a process of direct association of two equivalents of NMI to the

Table 3.11 NMR data of the mixtures of PhSiF₃ + r NMI in CDCl₃*.

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-F}}$ (Hz)	$\delta^{19}\text{F}$ (ppm)	$\delta^1\text{H}$ (NMI, ppm)***
0.0	-50.31, -65.34, -80.31, -95.35(q)	267.58	-141.55	(7.37, 6.96, 6.85, 3.53)
0.5	-83.61(br)	-	-137.21(br)	8.00, 7.16, 6.68, 3.44(br)
1.0	-110(vbr)	-	-128.93(br)	7.96, 7.17, 6.78, 3.48(br)
1.5	-140.8(vbr)	-	-122.39(br)	7.90, 7.14, 6.76, 3.44(br)
2.0	-155.5(vbr)	-	-119.43(br)	7.81, 7.11, 6.76, 3.43(br)
2.5	-159(vbr)	-	-188.80(br)	7.73, 7.08, 6.78, 3.44(br)
3.0	-167.9(vbr)	-	-118.51(br)	7.68, 7.05, 6.80, 3.44(br)
3.5	-169(vbr)	-	-118.27(br)	7.64, 7.04, 6.81, 3.44(br)
4.0	-171(vbr)	-	-118.04(br)	7.60, 6.98, 6.82, 3.45(br)
4.5	-172(vbr)	-	-117.93(br)	7.58, 6.93, 6.83, 3.45(br)
5.0	-172(vbr)	-	-117.81(br)	7.54, 7.00, 6.86, 3.46(br)
6.0	-172, -183(q,vbr)	207	-117.70(br)	7.56, 7.02, 6.84, 3.45(br)
7.0	-173, -184(q, vbr)	208	-117.52(br)	7.53, 6.99, 6.87, 3.46(br)
7.0 (at 220K)	-162.09, -174.04, -185.96, -197.98(q)	212.48	-107.10 (br,33%**) -121.29 (br,66%)	7.58, 7.02, 6.89, 3.43(br)

* c = 2.0 mmol./ml related to the silane.

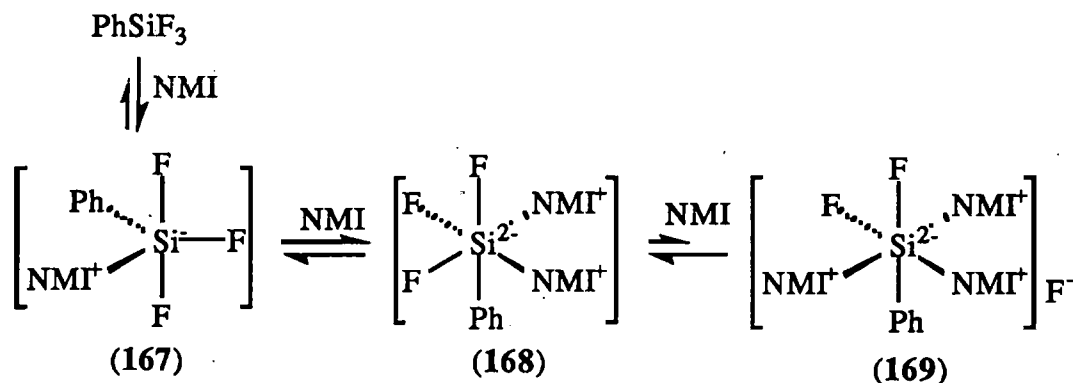
** The chemical shifts of ¹⁹F were related to CFCl₃ ($\delta^{19}\text{F}$ = 0.0 ppm); The percentages in brackets were the integrations of the signals hereinafter unless specified.

*** The proton shifts of the phenyl group were not listed as most of the signals were overlapping with those of NMI.

silane, finally forming a six-coordination complex without substitution any of the Si-F bonds.

In the ^{19}F NMR spectra, the additions of NMI made the chemical shifts move to low field from -141.55 ppm to about -118 ppm with broadened signals. However this deshielded signal was the result from fast intramolecular rotations of the Si-F bonds as indicated by low temperature study (220 K), in which the signal at -117.5 ppm split into two with a size ratio of about one to two, though it was still not low enough to observe the ^{19}F - ^{19}F coupling. The more shielded smaller one at -107.1 ppm and the less shielded larger one at -121.3 ppm correspond an octahedral hexacoordination. The chemical shifts of the broadened signals of the proton of NMI in the titration also verify the above rationalization.

The results of NMR study of the interaction of PhSiF_3 with NMI, therefore, can be expressed in Scheme 3.6, in which 168 is the most stable species.



Scheme 3.6 Reaction of PhSiF_3 with NMI.

$\text{PhSiF}_3 + \text{DMF}$ (or DMAP)

The addition of DMF into PhSiF_3 solution caused an immediate collapse of the ^{29}Si - ^{19}F coupling and the chemical shift of the ^{29}Si moved about 10 ppm to high field smoothly with the increases of the equivalents of DMF from one to five at room

temperature as shown in Table 3.12. As F^- is a poor leaving group and is proved to be reluctant to be replaced even by NMI, the high field shifted broadened ^{29}Si signal is probably the sign of a small amount of pentacoordinate species, like that of NMI with low equivalents ($r < 0.5$), in fast exchange with the silane. Although the 10 ppm high field shifts is not so significant, it is still large enough to indicate that PhSiF_3 is more reactive towards DMF at room temperature than PhSiCl_3 as hardly any alteration of the $\delta^{29}\text{Si}$ values were observed in the latter case. At low temperature, however, null ^{29}Si NMR signal was recorded for that of PhSiF_3 while hexacoordination was clearly indicated for that of PhSiCl_3 . Although the deshielded ^{19}F NMR signal at -139.3 ppm was split into two in a range between those of hexacoordination (-107 and -121 ppm) and that of tetracoordination (-141 ppm) at

Table 3.12 NMR data of the mixtures of $\text{PhSiF}_3 + r$ DMF in CDCl_3 .

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^{19}\text{F}$ (ppm)	$\delta^1\text{H}$ (ppm)	
			(PhSi)	(DMF)
1.0	-72.77(br)	-141.44(sbr)	7.68, 7.75	7.97, 2.87, 2.81(sbr)
2.0	-73.60(br)	-141.44(sbr)	7.69, 7.54	7.96, 2.88, 2.81(sbr)
3.0*	-76.56(br)	-140.57(sbr)	7.69, 7.53(sbr)	7.96, 2.89, 2.80(sbr)
4.0	-80.01(vbr)	-139.82(br)	7.70, 7.53(sbr)	7.97, 2.89, 2.80(sbr)
5.0	-82.16(vbr)	-139.29(br)	7.71, 7.51(sbr)	7.97, 2.90, 2.79(sbr)
5.0 (at 223K)	Null	-124.59 (br, 66%) -136.80 (sh, 33%)	7.75, 7.40(br)	8.00, 2.90, 2.80(sbr)

* CD_3CN added to dissolve the solid formed and the concentration was about 0.9 mmol/ml.

223 K, it is not certain whether a penta- or hexa-coordination was formed or even Si-F bonds substituted. Presumably DMF should react with PhSiF_3 in the same way as NMI and only has a smaller K. Therefore the split ^{19}F signals probably correspond a dominant species of pentacoordination like **167**, with two Si-F bonds in axial positions (-124.59 ppm) and one Si-F bond equatorial. The formation of hexacoordination is perhaps not so significant as DMF has such a low nucleophilicity.

Solids always formed with addition of PhSiF_3 into DMAP solution and the detailed reaction is not known.

$\text{PhSiF}_3 + \text{HMPA}$

The interaction of HMPA with PhSiF_3 is proved to be different from those of NMI and DMF by NMR studies as shown in Table 3.13.

In the ^{29}Si NMR spectra, the coupling of ^{29}Si - ^{19}F collapsed with the addition of HMPA and the broadened signal shifted gradually about 15 ppm high field with up to one equivalent of HMPA (see Entry 1 and 2 of Table 3.13). There were also alterations on the chemical shifts of ^{19}F , ^{31}P and ^1H . These observations indicate that a small quantity of pentacoordination similar to **167** formed and was in quite fast exchange with the silane.

However, further addition of HMPA to two equivalents made the ^{29}Si NMR signal disappear and the ^{19}F split into two at room temperature (see entry 3 of Table 3.13). The null ^{29}Si NMR was proved to be a triplet at a low field within the range of tetracoordination of -65.4 ppm with a ^{29}Si - ^{19}F coupling constant of 255 Hz by low temperature study (223 K). This means a tetracoordinated species was produced with one displacement of F^- by HMPA. The split ^{19}F NMR signal with about 60 percent intensity at -136.8 ppm corresponds the two Si-F bonds of the tetracoordinate adduct and the other more deshielded broadened signal with about 40 percent of intensity at -123.1 ppm comes from the fluoride ion. The chemical shift of the fluoride ion was checked with Bu_4NF , which comes at -124.1 ppm with broadened

Table 3.13 The NMR data of the mixtures of PhSiF₃ + r HMPA in CDCl₃.

	r	$\delta^{29}\text{Si}$	$J_{\text{Si-F}}$	$\delta^{19}\text{F}$	$\delta^{31}\text{P}$	$\delta^1\text{H}$ (ppm)	
		(ppm)	(Hz)	(ppm)	(ppm)	(PhSi)	(HMPA)
1	0.5	-77.02(br)	-	-139.7	26.72	7.65, 7.47	2.66, 2.55
2	1.0	-88.4(vbr)	-	-136.57	26.69	7.71, 7.45	2.64, 2.53
3	2.0	Null	-	-132.69 (br,40%) -137.73 (sbr,60%)	25.91	7.78, 7.39 (br)	2.63, 2.52 (br)
	LT*	-65.36(t,sbr)	255	-123.14(br)** -136.80	25.91	7.94, 7.43 (br)	2.59, 2.48 (br)
4	3.0	-65.53(t,br)	248	-130.26(br) -137.07	24.94	7.82, 7.39 (br)	2.64, 2.53 (br)
5	4.0	-65(t,br)	nr	-129.69(br) -137.56	24.23	7.77, 7.38 (br)	2.64, 2.54 (br)
6	5.0	-65.45(t,br)	245	-129.11(br) -137.50	23.69	7.78, 7.38 (br)	2.65, 2.54 (br)
	LT*	-65.20(t,sbr)	254	-121.92(br) -136.40	23.19	7.80, 7.39 (vbr)	2.63, 2.53 (vbr)

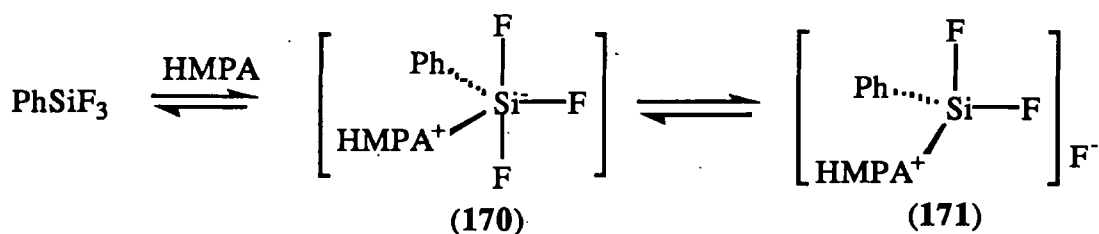
* LT means the NMR was run at low temperature (223 K). (c = 1.0 mmol./ml to PhSiF₃).

** The relative intensities of the ¹⁹F signals were not listed as they remained the same.

shape. Therefore the formation of monosubstituted tetracoordinate adduct is quite certain and this adduct is rather inert to further chemical reaction with HMPA as the increases of the equivalents of HMPA to five, even at low temperature (223 K), have hardly made any significant changes on the chemical shifts and the line shapes of ²⁹Si, ¹⁹F and ¹H as well as the coupling of ²⁹Si with ¹⁹F of the silyl moiety.

Nonetheless the adduct was undergoing exchanges with the free fluoride ion and HMPA as a chemical equilibrium usually does, which is indicated by the broadened signals of the protons and the slightly shielded fluoride signal at room temperature.

Therefore the interaction of HMPA with PhSiF_3 in solution is a monosubstitution process by pentacoordination as shown in Scheme 3.7.



Scheme 3.7. Reaction of PhSiF_3 with HMPA.

$\text{PhSiF}_3 + \text{DMPU}$

The interaction of weak nucleophile DMPU with PhSiF_3 in solution examined by NMR is comparable with that of DMF in reactivity as shown in Table 3.14.

The addition of DMPU in PhSiF_3 solution up to one equivalent had hardly caused any change of the NMR signals of ^{29}Si , ^{19}F and ^1H of the silane. However, further addition of DMPU caused the collapse of the ^{29}Si - ^{19}F coupling producing a broadened signal and the chemical shift of silicon-29 moved slowly to high field together with the deshielding of ^{19}F as the equivalents of DMPU increased. With five equivalents of DMPU present at room temperature the $\delta^{29}\text{Si}$ value shifted to -82.5 ppm with a very broadened signal, which moved further to -95.5 ppm with improved sharpness at low temperature. These observations indicate the formation of pentacoordinate species in the mixture and which, probably, became the dominant species at low temperature (223 K) with high proportion of DMPU ($r = 5$). Nonetheless, only one ^{19}F signal was observed even at low temperature, though progressively deshielded. This means the pentacoordination was undergoing a very fast intramolecular exchange, *eg.*

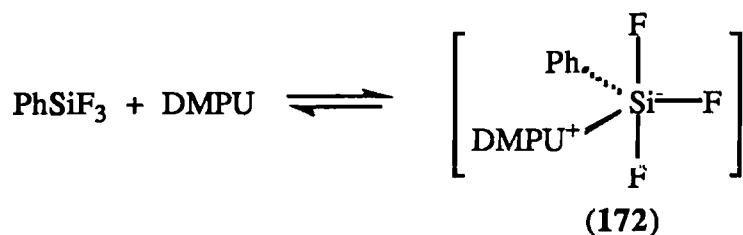
Table 3.14 The NMR data of the mixtures of PhSiF₃ + r DMPU in CDCl₃.

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^{19}\text{F}$ (ppm)	$\delta^1\text{H}$ (ppm)	
			(PhSi)	(DMPU)
1.0	-72.2(q)	-141.38	7.64, 7.50	3.16(t), 2.89, 1.87(qu)
2.0	-73.02(sbr)	-141.03	7.65, 7.53	3.17(t), 2.88, 1.89(qu)
3.0	-76.40(sbr)	-139.29	7.68, 7.53	3.19(t), 2.87, 1.89(qu)
4.0	-79.85(br)	-137.73	7.71, 7.53	3.19(t), 2.86, 1.89(qu)
5.0	-82.5(vbr)	-136.75	7.71, 7.53	3.20(t), 2.85, 1.90(qu)
5.0(223K)	-95.49(br)	-132.29	7.82, 7.33	3.15, 2.85, 1.86(all br)

c = 1.1 mmol./ml relative to the silane.

pseudorotation, and intermolecular exchange involving the pentacoordinated species. The proton signals of the mixtures, especially the increased separation of the two sets of multiplets of the phenyl group at low temperature, agree with such a rationalization. No evidence of hexacoordination or mono-substituted tetracoordination was found.

Therefore the interaction of DMPU with PhSiF₃ is only a process of direct association with one equivalent DMPU to form pentacoordination as shown in Equation 3.1.



Equation 3.1

3.3.3 Summary

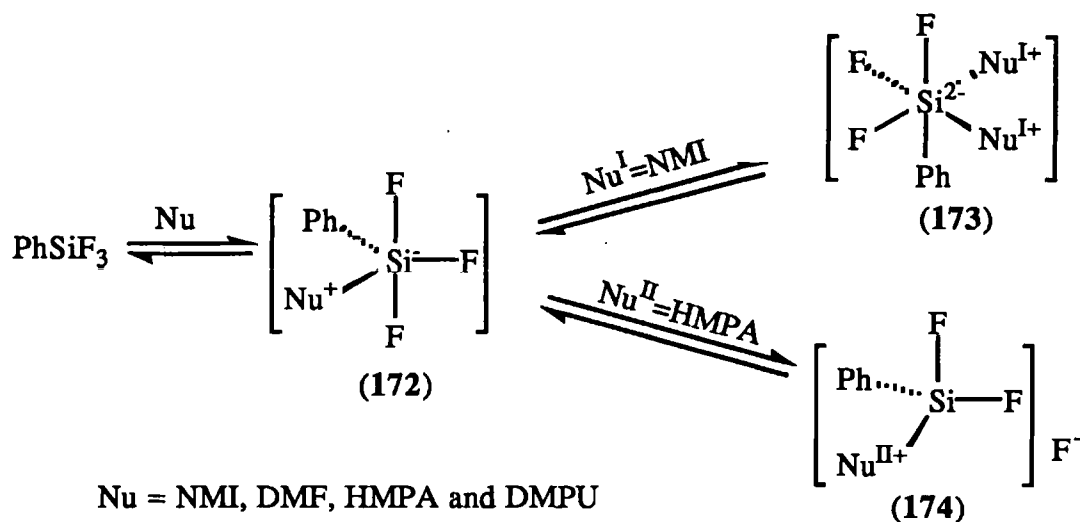
The coordination chemistry and nucleophilic substitution mechanisms of the interactions of phenyltrifunctional silanes PhSiX_3 ($X = \text{F}, \text{Cl}$) with nucleophiles in solution examined by ^{29}Si , ^{19}F , ^{31}P and ^1H NMR and conductivity studies depend on the electronic and steric properties of both the nucleophiles and the leaving groups.

Generally speaking, nucleophiles with small steric hindrance upon complexation (Nu^{I} , including NMI, DMAP and DMF) ultimately form complexes with PhSiX_3 of a higher coordination number than those spatially demanding nucleophiles (Nu^{II} , including HMPA and DMPU). The highest coordination number at silicon observed with PhSiX_3 and neutral nucleophiles is six, presented by Nu^{I} such as NMI, and the lowest is four, represented by PhSiF_3 with HMPA.

The nucleophilicity of the nucleophiles, measured by Taft's Beta values (β), contributes to the equilibrium constant K significantly; the higher the Beta value, the larger the K . Therefore weak nucleophiles (small β , such as DMF and DMPU) seemingly have a less complicated reaction with PhSiX_3 as they are too weak to push the equilibria to complexation.

The leaving groups affect the coordination chemistry and the nucleophilic reaction pathways at silicon by their electronegativity and their leaving ability. The more electronegative and the more reluctant to leave of the leaving groups, the higher the coordination number at silicon of the silane-nucleophile complexes except PhSiF_3 with HMPA.

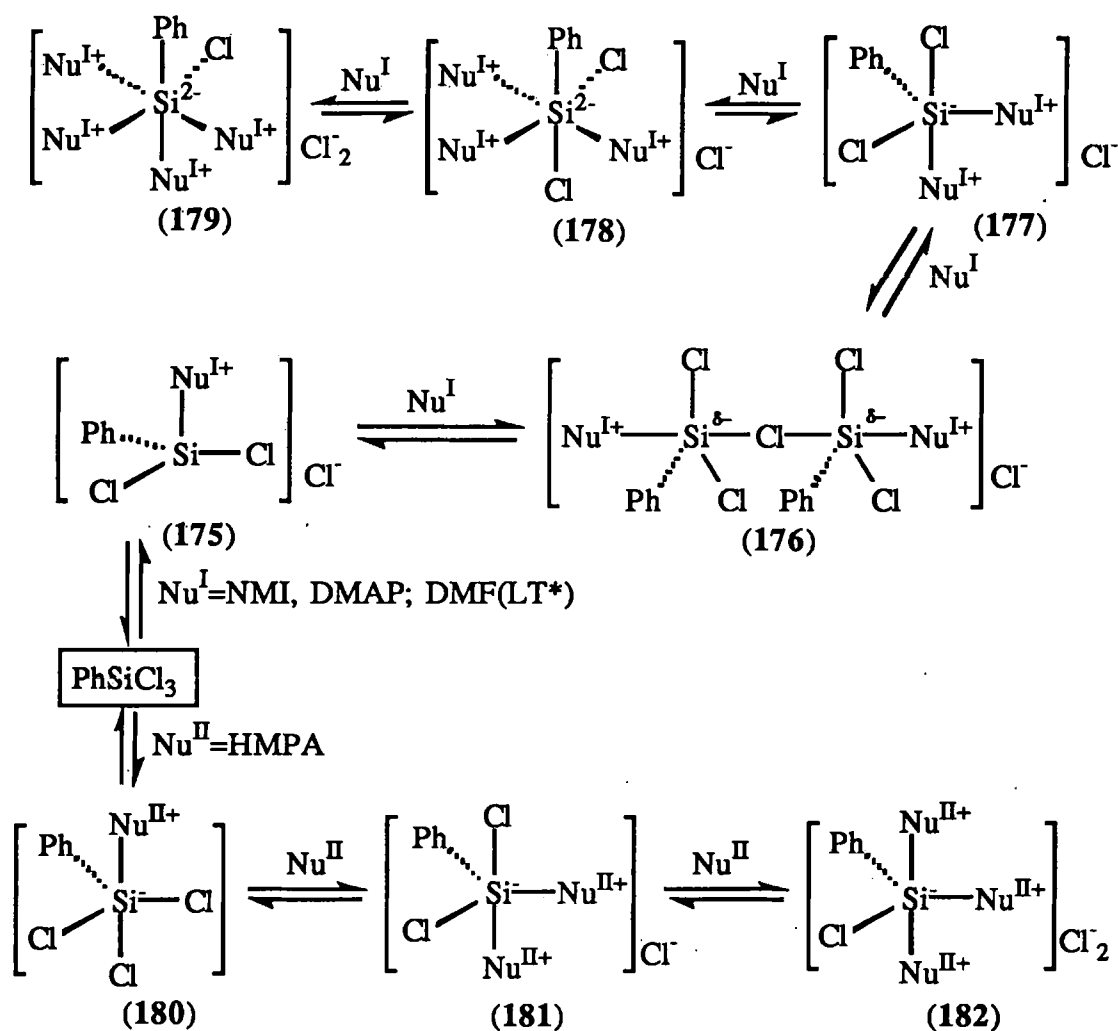
Fluorine, as a poor leaving group, leads PhSiF_3 to associate directly with one equivalent of nucleophile to increase its coordination to five (172) as shown in the first step in Scheme 3.8. With strong and sterically favourable nucleophiles, such as NMI, the pentacoordination can be further increased to hexacoordination (173) while strong but spatially demanding nucleophiles, such as HMPA, will collapse the pentacoordinate structure resulting in a monosubstituted tetracoordinate adduct



Scheme 3.8 Summary of the interactions of PhSiF₃ with nucleophiles.

(174). The further reaction of 173 and 174 with the corresponding nucleophiles is insignificant. Presumably the species 172 of DMF and DMPU could further react in similar ways according to their steric properties but no evidence was found for reaction beyond 172 as they are too weak nucleophiles to bring the reaction to similar results.

Chlorine, being a less electronegative and a better leaving group than fluorine, causes the reactions of PhSiCl₃ with nucleophiles to take different routes from those of PhSiF₃ according to the steric properties of the nucleophiles as shown in Scheme 3.9. These reaction pathways are very similar to those of MeSiCl₃. With less spacially demanding nucleophiles, such as NMI, DMAP and DMF, PhSiCl₃ will produce a monosubstituted tetracoordinate adduct 175 at the first step and followed by pentacoordinate intermediates 176 and 177 leading to hexacoordination 178 and 179. With spacially demanding nucleophiles, such as HMPA, PhSiCl₃ forms only pentacoordination 180, 181 and 182. There is no definite information on whether the final hexacoordinate complexes retain any Si-Cl bonds or whether they have all been substituted by nucleophiles. There is hardly any significant reaction observed with weak nucleophiles such as DMPU.



Scheme 3.9 Summary of the interactions of PhSiCl₃ with nucleophiles.

* LT, at low temperature (223 K).

The leaving ability and electronegativity of the leaving groups also contribute to the reactivity of PhSiX₃ (X = F, Cl). The reason PhSiF₃ is more reactive to DMPU than PhSiCl₃ is probably that fluorine is more electronegative, which leads the silicon to be more electropositive and therefore to be more readily attacked by nucleophiles.

However the substitution of the functional groups other than the reactivity of the silanes is mainly a property of the leaving ability of the leaving group. Therefore Si-Cl bonds are more easily displaced by nucleophiles such as NMI and HMPA as Cl⁻ is a better leaving group than F⁻.

3.4 The interaction of HSiX_3 ($\text{X} = \text{Cl}, \text{OTf}$) with nucleophiles

H-containing difunctional silanes RHSiX_2 have shown that they are more readily to increase coordination at silicon and have their own particular coordination chemistry and reaction pathways with nucleophiles because of the small size of hydrogen, as stated in Chapter 2. In this subsection the effects of a replacement of alkyl or aryl group by hydrogen of trifunctional silanes are discussed.

3.4.1 The interactions of HSiCl_3 with nucleophiles

The coordination chemistry and reaction pathways of multifunctional silanes with nucleophiles are very much dependent on the steric effects from both the silanes and the nucleophiles. The discussion of the interactions of HSiCl_3 with nucleophiles is described according to the possible steric hindrance of the nucleophiles upon complexation.

$\text{HSiCl}_3 + \text{NMI}$

The interactions of HSiX_3 ($\text{X} = \text{Cl}, \text{OTf}$) with nucleophiles are more complicated as the silanes are more reactive. However the examination of the reaction between HSiCl_3 and NMI in solution by ^{29}Si NMR has clearly shown a formation of hexacoordinated silicon species in the equilibrium. Some of the typical NMR data of the mixtures in a mixture solvent are listed in Table 3.15. In the presence of 0.95 equivalents of NMI, a small but sharp ^{29}Si resonance signal besides the large one of HSiCl_3 was observed at a high field of -184.47 ppm, more than 175 ppm away from that of the silane, together with a decreased ^{29}Si - ^1H coupling constant of 303.7 Hz, which indicates a small amounts of hexacoordinate species were in slow exchange in the solution. The size of this high field signal became larger as the signal of the silane diminished with the increases of equivalents of NMI up to 2.85, but the value of chemical shift remained unchanged even with large equivalents of NMI (see Entry 6

Table 3.15 NMR data of the mixtures of $\text{HSiCl}_3 + r \text{ NMI}^*$.

	r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}$ (ppm)		Note
				(HSi)	(NMI)	
	0.0	-9.30	372.2	6.16	(7.37, 6.96, 6.85, 3.53)	
1	0.95	-9.89(l**) -184.47	372.2 303.7	5.57, 5.90, 6.16(l)	8.89(vbr); 9.10, 7.42, 7.20, 3.88(sbr)	
2	1.90	-11(br) -184.40	372.2 305.2	5.69, 5.90, 6.16(l,br)	8.8(vbr); 9.11, 7.42, 7.28, 3.89(sbr)	
3	2.85	-184.40	305.2	5.82, 5.90, 6.05(br)	8.8(vbr); 9.14, 7.42, 7.37, 3.91(sbr)	
4	4.75	-184.45	288.5	5.94	8.0, 7.2(vbr); 9.28, 7.49, 3.93(sbr), 3.84(s)	
5	5.00	-184.40	288.6	5.94	7.9, 7.0(vbr); 9.40, 7.44 3.95(sbr), 3.78(s)	
		-184.40	287.1	5.93	7.8, 7.0(vbr); 9.17, 7.44, 7.24, 3.91(sbr), 3.79(s)	c= 0.25
		-184.46	288.6	5.91	7.9,7.1(vbr); 9.12, 7.45, 7.26, 3.90(sbr), 3.80(s)	at 220K c=0.25
6	6.65	-184.45	290.9	5.95	7.8, 7.1(vbr); 9.31, 7.47, 3.90(sbr), 3.75(l)	

* c = 1.0 mmol./ml related to the silane in $\text{CD}_3\text{CN} + \text{CDCl}_3$ unless specified.

** l and s mean the size of the signal is at least 60% larger or smaller than the related other signals; the size is normal or about the same if not specified.

of Table 3.15) or in a solution diluted by four times and at low temperature (see Entry 5 of Table 3.15). Nonetheless there is a decrease of about 17 Hz in the coupling of $^{29}\text{Si}-^1\text{H}$ between 2.85 and 4.75 equivalents of NMI. Therefore there may

be a substitution within the hexacoordination even the chemical shift of ^{29}Si remained unchanged.

In the ^1H NMR spectra, the three signals of the HSi moiety with up to 2.85 equivalents of NMI suggest there are three silyl species in exchange, one from HSiCl_3 (6.16 ppm) and the others from the adducts, probably the hexacoordination (5.90 ppm) and perhaps a pentacoordinate intermediate. These signals became a single one and remained as NMI reached 4.75 equivalents. The signals of NMI moiety, though complicated, also displayed a changed pattern when NMI increased from 2.85 to 4.75 equivalents. Therefore it is more likely that a substitution process exists within the hexacoordinate structure.

In fact a solid adduct was isolated from a reaction mixture in CHCl_3 and was found to have the formula of $\text{HSiCl}_3 \cdot 3 \text{ NMI}$ by elemental analysis and solution NMR, which indicated that at least one Si-Cl bond was probably substituted.

$\text{HSiCl}_3 + \text{DMAP}$

Hexacoordination is also observed by NMR with the interaction of HSiCl_3 with DMAP in dilute solution of CD_3CN and CDCl_3 . A sharp ^{29}Si resonance signal at a high field of -150.98 ppm was recorded with 6.3 equivalents of DMAP present. The coupling of ^{29}Si - ^1H decreased to 303.3 Hz as well. In the ^1H NMR spectrum, the SiH proton was shielded to 5.33 ppm and the protons of DMAP had two sets of signals deshielded. Therefore the final products of the interaction of DMAP with HSiCl_3 are, most likely, very similar to those of NMI with HSiCl_3 .

$\text{HSiCl}_3 + \text{DMF}$

In principle, the weak nucleophile DMF could react with HSiCl_3 in the way of NMI and DMAP. However the addition of DMF into HSiCl_3 solution released gas. NMR examination of the mixtures showed that the Si-H bond was largely decomposed as illustrated in Table 3.16. Although there were ^{29}Si resonance signals at about -34, -184 and -192 ppm, the large ^{29}Si - ^1H couplings, that is the indication of Si-H bonds,

Table 3.16 NMR data of the mixtures of $\text{HSiCl}_3 + r \text{ DMF}$ in CDCl_3

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}(\text{ppm})$	
			(HSi)	(DMF)
1.56	-11.85(s)	363.4	6.15	9.60, 9.40, 8.75; 3.63, 3.33, 3.09
3.12	-34.99, -184.73, -192.05 Null	<3(all) Null	6.11 (s br)	9.56, 9.25, 8.76; 3.63, 3.31, 3.15
4.68	-34.74, -184.73, -192.05 -165.79	<3 332.6	nr	9.53, 9.23; 8.11(s); 3.62, 3.31; 3.06, 2.99
7.80	-34.33, -184.73, -192.22 -166.78(s,sh)	<3 329.7	nr	9.95, 9.24; 8.07(l); 3.64, 3.34(s); 3.02, 2.86

c = 1.0 mmol./ml related to HSiCl_3 .

disappeared. The proton signals of the Si-H bond also diminished and those of DMF were complicated in the ^1H NMR spectra. Nevertheless, there were still a small amounts of Si-H bond remaining, which indeed formed hexacoordination with DMF indicated by a high field ^{29}Si chemical shift to about -167 ppm with a decreased ^{29}Si - ^1H coupling to about 330 Hz as the proportion of DMF increased ($r \geq 4.68$). The increase of coordination at silicon and the decomposition of the Si-H bond may be through a common intermediate, namely a pentacoordinate species in which one of DMF is directly associated with the silicon. Anyway, the detailed mechanism is impossible to understand with such a simple example.

Conductivity studies of $\text{HSiCl}_3 + \text{NMI}$ (or DMAP or DMF)

Conductivity measurements of the mixtures of HSiCl_3 with NMI, DMAP and DMF in solution have shown that the concentrations of ionic species in these system are quite low. The titration curves of HSiCl_3 with NMI and DMF against conductivity

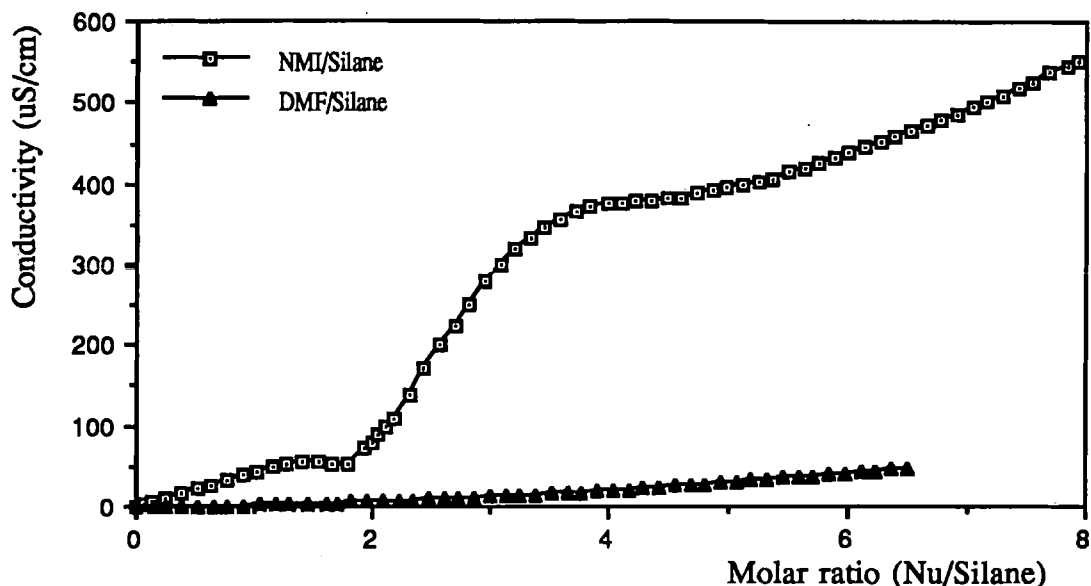


Figure 3.7 Conductivity titrations of HSiCl_3 with NMI and DMF.

The concentration was 0.15 mmol./ml related to the silane in both titrations in CHCl_3 (0.5 ml CH_3CN was added in the titration with NMI).

are illustrated in Figure 3.7.

The conductivity of the HSiCl_3 solution only slightly increased with the addition of NMI up to two equivalents. This suggests NMI is largely associated to silicon directly, forming hypercoordination without significantly producing free ions. The larger increases of conductivity as the amount of NMI increased from two to four equivalents corresponds to substitutions of chlorine by NMI within the hexacoordination as proposed in NMR study. The relatively small conductivity readings and the small increases with high equivalents of NMI ($r \geq 4$) suggest that probably only one chloride ion is displaced.

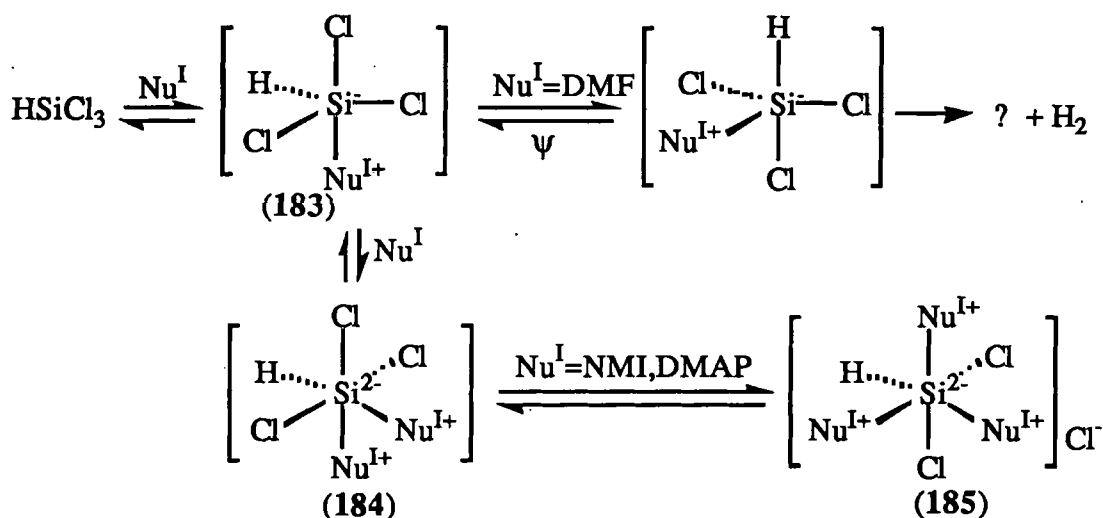
The conductivity reading of the titration of DMAP with HSiCl_3 in CHCl_3 is not so large either. The highest reading is just $137.5 \mu\text{S/cm}$ ($c = 0.3 \text{ mmol./ml}$ relative to DMAP). Therefore the substitution of chlorine by DMAP is also one at most.

The conductivity of the mixtures of DMF with HSiCl_3 is even smaller, though the decomposition of the Si-H bonds is the dominant process as gas production was

observed. Therefore there might be no ions formed.

Summary

The results of NMR and conductivity studies of the interactions of HSiCl_3 with NMI, DMAP and DMF (Nu^{I}) in solution show that hexacoordination is formed, probably by way of pentacoordination as illustrated in Scheme 3.10.



Scheme 3.10 Summary of the interactions of HSiCl_3 with Nu^{I} .

$\text{HSiCl}_3 + \text{HMPA}$

The contribution of Nu^{II} , represented by HMPA and DMPU, to the coordination number at silicon in nucleophilic reactions has always been different from that of Nu^{I} such as NMI, DMAP and DMF as stated above. However the coordination of the interaction of HSiCl_3 with HMPA in solution has shown little difference between the two categories as illustrated in Table 3.17.

In the ^{29}Si NMR spectra, a main signal shifted progressively to high field, from -109.9 to -188.2 ppm, together with a ^{29}Si - ^1H coupling between 405 to 408 Hz as the equivalents of HMPA increased, though a null signal was recorded with 1.1

Table 3.17 NMR data of the mixtures of $\text{HSiCl}_3 + r \text{ HMPA}$.

	r	$\delta^{29}\text{Si}$	$J_{\text{Si-H}}$	$\delta^{31}\text{P}$	$\delta^1\text{H}$ (ppm)	
		(ppm)	(Hz)	(ppm)	(HSi)	(HMPA)
1	1.1	Null -71.6(s, t, vbr)	Null 337.5	26.5(br)	6.04, 5.81(s)	2.83, 2.71(sbr)
2	2.0	-109.90(br) -90.3(s, t, vbr)	405.9 346.6	26.09(br)	5.93, 5.62(s)	2.84, 2.72(sbr)
3	3.2	-153.70(br) -98.9(s, t, vbr)	408.8 344.4	26.06(sbr)	5.77, 5.46(s)	2.82, 2.71(sbr)
4	4.5	-175.92(sbr) -100(s, t, vbr)	407.4 342.9	26.9(sbr)	5.68, 5.37(vs)*	2.80, 2.69(sbr)
5	5.8	-184.56 -101(vs, t)	407.3 342.9	26.7(sbr)	5.65 nr	2.78, 2.67(sbr)
6	6.8	-188.23(sh)	405.8	27.4(sbr)	5.62	2.76, 2.65(sbr)

c = 0.5 mmol./ml related to HSiCl_3 in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

* vs, very small

equivalents of HMPA. This suggests HSiCl_3 also forms hexacoordinate complexes with HMPA by way of pentacoordination, probably direct association without substitution. The increases of the coordination with HMPA in this case is because only the small-sized hydrogen is bonded to silicon besides the functional groups, and this reduces the steric hindrance relative to R groups such as methyl and phenyl.

In addition, there was a very small and extremely broadened signal shifted to high field, appearing, from -71.6 to -101 ppm. But the ^{29}Si - ^1H coupling of this signal was

shown by ^{29}Si INEPT to be triplet and indicated a small amount of dihydridosilyl H_2Si species was produced. Such disproportionation reaction of HSiCl_3 in the presence of HMPA can probably be attributed to the formation of pentacoordinate intermediate, by which the Si-H bond was activated through pseudorotation to the more loosely bonded to apical positions as steric hindrance is reduced.

In the ^1H NMR spectra, there were also two sets of signals increasingly shielded corresponding to the Si-H bonds, one from the HSiCl_3 moiety the other from H_2Si . The slightly broadened proton signals of HMPA, together with the slightly broadened ^{31}P signals from the ^{31}P NMR spectra, showed that HMPA was in exchanges with the coordinated species.

Therefore the interaction of HMPA with HSiCl_3 forms hexacoordination at silicon by way of pentacoordination, disproportionation of the pentacoordinate intermediate is also possible.

$\text{HSiCl}_3 + \text{DMPU}$

The interaction of HSiCl_3 with the spacially demanding but weak nucleophile DMPU proceeds similarly to that of HMPA, but only pentacoordination is produced due to the poor nucleophilicity of DMPU as is shown by the NMR data in Table 3.18.

The main ^{29}Si resonance signal of the mixtures of HSiCl_3 with DMPU shifted progressively to high field together with gradually increased ^{29}Si - ^1H coupling as the equivalents of DMPU increased, reaching -101.3 ppm with a quite sharp signal and a coupling of 417.6 Hz when $r=9.0$. This is in the range of pentacoordinate silicon.

What is interesting is that a small resonance signal appeared in both ^{29}Si and ^1H NMR spectra as the amount of pentacoordination of HSiCl_3 with DMPU became measurable ($r \geq 2$). This new ^{29}Si NMR signal was a triplet in the ^{29}Si INEPT spectrum with a ^{29}Si - ^1H coupling reading from 341 to 348 Hz and shifted to high field as the equivalents of DMPU increased just as in the case with HMPA. These

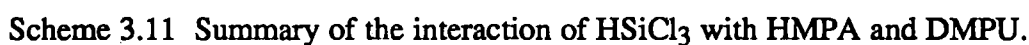
Table 3.18 NMR data of the mixtures of $\text{HSiCl}_3 + r$ DMPU in CDCl_3 .

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}$ (ppm)	
			(HSi)	(DMPU)
1.0	-13.25	369.3	6.17	3.28(t), 2.94, 1.99
2.0	-30.54(sbr)	381.0	6.26 5.81(s)	3.32(t), 2.96, 2.01(qu)
3.0	-59.43(br) -70.48(s, t, vbr)	nr 340.7	6.36 5.86(s)	3.35, 2.97, 2.04(qu)
5.0	-88.00(br) -89.69(s, t, vbr)	413.2 346.6	6.47 5.90(s)	3.35(t), 2.93, 2.01(qu)
7.0	-96.56 -92.48(s, t, vbr)	416.1 348.0	6.53	3.33(t), 2.92, 1.99(qu)
9.0	-101.34(sh)	417.6	6.53	3.31(t), 2.91, 1.99(qu)

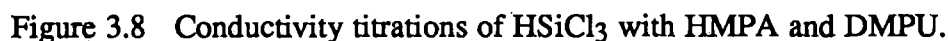
c = 0.8 mmol./ml related to HSiCl_3 .

observations indicate that disproportionation reaction of HSiCl_3 also took place with DMPU and happened by way of pentacoordination.

Therefore the interactions of HMPA and DMPU with HSiCl_3 may proceed in the same way as illustrated in Scheme 3.11. Both involved some disproportionation of HSiCl_3 , possibly through a pentacoordinated intermediate **186**. The only exception is that HMPA forms hexacoordinate species **188**, **189** and perhaps **190** with HSiCl_3 when the equivalents of HMPA increase. This results from the stronger nucleophilicity of HMPA and the reduced steric hindrance at the silyl moiety due to the hydrogen atom.



The conductivity measurements of the mixtures of HSiCl_3 with HMPA or DMPU in solution were complicated as a results of the disproportionation reaction of HSiCl_3 . However, as demonstrated in Figure 3.8, the conductivity titrations of HSiCl_3



c = 0.11 and 0.15 mmol./ml related to the silane respectively to the titration of HMPA and DMPU in mixture solvent of CH₃CN and CHCl₃

solution with the nucleophiles have showed that no significant ionic species were produced until the molar ratios of nucleophile to silane were greater than two. This agrees with the formation of the neutral pentacoordinated complex **186** observed by NMR study of the reactions. For HMPA there was a significant conductivity increase when the equivalents of the nucleophile was more than two, which indicated the production of ions by way of **188** to **189** or even to **190**. For DMPU the smaller conductivity increases with more than two equivalents of the nucleophile may be contribute either due to a small amount of substituted species or to the interference of the partial disproportionation reaction of HSiCl_3 .

3.4.2 The interaction of HSiOTf_3 with nucleophiles

HSiOTf_3 is extremely moisture sensitive and is the most reactive silane dealt with in this study. The examination of the interactions of HSiOTf_3 with nucleophiles by NMR were further complicated, especially in the proton spectra, by the presence of about ten percent impurity of PhHSiOTf_2 in the silane. Nonetheless the coordination chemistry of silicon of the mixtures of HSiOTf_3 with nucleophiles can still be clarified by the distinctive chemical shifts in the silicon-29 NMR spectra.

$\text{HSiOTf}_3 + \text{NMI}$

The ^{29}Si chemical shifts of the mixtures of HSiOTf_3 with NMI as shown in Table 3.19 were in the range between -186 to -198.3 ppm with a decreased ^{29}Si - ^1H coupling to about 318 Hz. Such a high field shift definitely suggests the formation of hexacoordinate silicon without any significant existence of pentacoordination. However the interpretation of the substitution of the triflate groups is difficult. All these ^{29}Si NMR signals were sharp. Although the absolute $\delta^{29}\text{Si}$ values tend to decrease with the increase of the equivalents of NMI from one to eight, the double signals with one equivalent NMI at the highest field is not readily explained. The limited information in the proton spectra is that some of the triflate groups must have displaced as there was a dramatic change of the chemical shift of Si-H proton from a

Table 3.19 NMR data of the mixtures of HSiOTf₃ + r NMI

	r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}(\text{ppm})$		Note
				(HSi)	(NMI)	
1	0.0	-76.15	416.0	5.46	(7.37, 6.96, 6.85, 3.53)	in CDCl ₃
2	1.0	-194.65 -198.31	385.3 411.0	4.93 (sbr)	8.22, 8.03, 7.12, 7.77, 3.83, 3.77	CD ₃ CN added
3	2.0	-188.60 -189.50	nr nr	4.97 (sbr)	8.27, 8.20, 8.09, 7.15, 7.05, 3.81, 3.80	
4	3.0	-186.87 -188.43(l)	nr nr	nr	nr	
5	5.0	-185.96	319.3	5.93 (sbr)	8.52(s), 8.01, 7.40, 7.23, 7.10, 6.92, 3.76(br)	c=0.76
6		-186.70	317.9	6.01 (sbr)	8.15(s), 7.92, 7.82, 7.51, 7.25, 7.19, 6.75, 6.73, 3.87(s), 3.78, 3.75	c=0.19
7		-187.52	nr	5.93 (sbr)	8.13(s), 7.80, 7.55, 7.28, 7.14, 3.87(s), 3.77	225 K c=0.19
8	8.0	-186.45	317.9	6.14 (sbr)	8.53(s), 8.04, 7.67, 7.04, 6.95, 3.90, 3.86, 3.77, 3.67(l)	

c = 0.5 mmol./ml related to the silane (assumed to be 100% HSiOTf₃ though PhHSiOTf₂ was present in small amounts) in CD₃CN + CDCl₃ unless specified.

shielded position 4.97 ppm to a deshielded position 5.93 ppm when the equivalents of NMI increased from two to five. The proton signals of NMI were complicated and only indicated that NMI was involved in complexation. Nonetheless a solid adduct separated from the mixture was found by elemental analysis to have a formula of $\text{HSiOTf}_3 \cdot 5 \text{ NMI}$, which has a $\delta^{29}\text{Si}$ value of -186.21 ppm with a ^{29}Si - ^1H coupling of 319.3 Hz. Therefore the interaction of HSiOTf_3 with NMI produces only hexacoordination, by which substitutions of the triflate groups by NMI take place as shown in Equation 3.1.



Equation 3.5

$\text{HSiOTf}_3 + \text{DMAP}$ (or DMF)

The interactions of DMAP or DMF with HSiOTf_3 examined by NMR are more or less the same as that of NMI. Some of the typical NMR data are collected in Table 3.20.

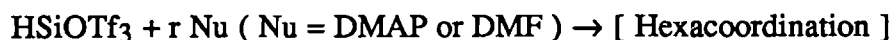
The addition of the first equivalent of nucleophiles immediately moved the ^{29}Si chemical shifts to a high field between -180.9 to -202.0 ppm with two or three signals. These signals shifted downfield on increasing the equivalents of the nucleophile but remained in the range of hexacoordinate silicon, which indicates the substitution of the triflate groups. Although null ^{29}Si resonance signal was recorded with eight equivalents of nucleophile (either DMAP or DMF), probably because of intermediate exchanges among those species involved, there was no evidence of pentacoordination. Therefore the interactions of HSiOTf_3 with either DMAP or DMF also promote hexacoordination and the substitution of the triflate groups by the nucleophile proceeds within hexacoordinate complexes as shown in Equation 3.2.

Table 3.20 NMR data of the mixtures of HSiOTf₃ + r DMAP (or r DMF)

r	HSiOTf ₃ + r DMAP			HSiOTf ₃ + r DMF		
	$\delta^{29}\text{Si}$	$J_{\text{Si-H}}$	$\delta^1\text{H}(\text{SiH})$	$\delta^{29}\text{Si}$	$J_{\text{Si-H}}$	$\delta^1\text{H}(\text{SiH})$
1.0	-185.96 -194.52	395.5 421.9	6.04, 4.64	-180.94, -190.41(1) -202.01	385.3 391.1 416.1	5.70, 4.48
2.0	-166.49	323.8	6.05, 4.93	-173.9, -179.3	367.8, 386.8	4.47, 4.41
3.0	-156.0 -166.33	271.1 318.0	6.27, 5.33	-	-	-
5.0	-166.49	323.8	5.90, 5.30	-	-	-
8.0	Null	Null	5.85, 5.30	Null	Null	nr

The concentration was 1.2 mmol./ml related to DMAP in its titrations with HSiOTf₃ in

CD₃CN + CDCl₃ and 0.7 mmol./ml related to the silane in its titration with DMF in CDCl₃.



Equation 3.2

HSiOTf₃ + HMPA

The interactions of HSiOTf₃ with spacially demanding nucleophiles such as HMPA and DMPU proceed in a different way. The addition of HMPA into HSiOTf₃ solution does not produce hexacoordination but pentacoordination even with two equivalents

Table 3.21 NMR data of the mixtures of HSiOTf₃ + r HMPA.

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^{31}\text{P}$ (ppm)	$\delta^1\text{H}$ (ppm)	
				(HSi)	(HMPA)
1.0	-134.59	435.3	26.52(sbr)	5.51	2.80, 2.68(br)
	-142.50(s)	442.6		5.40(s)	
2.0	-134.62	435.3	26.22	5.50(s)	2.83, 2.71(sbr)
3.0	Null	Null	29(vbr)	5.46(s)	2.83, 2.71(sbr)
4.2	Null	Null	27.86	5.45(s)	2.76, 2.65
6.0	Null	Null	26.89	5.46(s)	2.73, 2.62
8.0	-108.09	662.3	26.62	5.01(s)	2.72, 2.61

c = 0.4 mmol./ml related to the silane in CD₃CN + CDCl₃.

of HMPA present as shown in Table 3.21. The ^{29}Si chemical shift of -134.6 ppm with a ^{29}Si - ^1H coupling of 435.3 Hz was unchanged when the ratio of HMPA to silane increased from one to two, though the intensity reduced. The smaller signal at -142.5 ppm with a coupling of 442.6 Hz may come from a similar adduct with different configuration. These signals are in the range of pentacoordinate silicon. No evidence of hexacoordination was found with further addition of HMPA up to eight equivalents. Instead a weak but sharp signal at -108.09 ppm, which was a triplet in the ^{29}Si INEPT spectrum with a ^{29}Si - ^1H coupling of 331 Hz, was recorded. This new signal corresponds to a dihydridosilyl species as has been seen in the interaction of HSiCl₃ with HMPA or DMPU. The failure of HSiOTf₃ to form hexacoordination with HMPA as HSiCl₃ does probably results from steric hindrance of the bigger size of the triflate groups. Therefore the disproportionation reaction by pentacoordination of HSiOTf₃ is

the predominant result in the presence of HMPA; that is :



Equation 3.3

HSiOTf₃ + DMPU

The NMR study of the interaction of HSiOTf₃ with DMPU is very similar to that with HMPA initially, as illustrated in Table 3.22. There were also two signals of -132.9

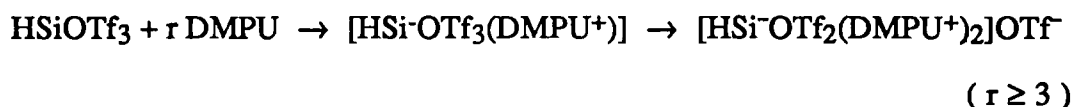
Table 3.22 The NMR data of the mixtures of HSiOTf₃ + r DMPU.

r	$\delta^{29}\text{Si}$ (ppm)	$J_{\text{Si-H}}$ (Hz)	$\delta^1\text{H}$ (ppm)	
			(HSi)	(DMPU)
1.0	-132.87, -134.02(s)	417.7 436.7	5.46 5.40(s)	3.55, 3.17, 2.13(sbr)
2.0	-131.96(br)	398.6	5.46	3.57, 3.14, 2.12(br)
3.0	-133.11(sh)	382.5	5.41	3.55, 3.11, 2.12(sbr)
7.0	-133.28(sh)	378.1	5.42(sbr)	3.37, 2.94, 2.06(br)

c = 0.5 mmol/ml related to the silane in CD₃CN + CDCl₃.

and -134.0 ppm in the ²⁹Si spectra with ²⁹Si-¹H couplings of 417.7 and 436.7 Hz respectively when one equivalent nucleophile DMPU was present. However there was no sign of disproportionation reaction of HSiOTf₃ with further addition of DMPU. Instead a sharp resonance signal at -133 ppm with a coupling of ²⁹Si-¹H about 380 Hz appeared with equivalents of DMPU from three to seven after a broadened signal

around -132 ppm with two equivalents of DMPU, which probably indicates a substitution of the triflate groups by DMPU without changing the coordination at silicon. All these ^{29}Si chemical shift values are in the range for pentacoordination at silicon. No evidence of hexacoordination was found. Therefore the interaction of DMPU with HSiOTf_3 is different with those of Nu^{I} (NMI, DMAP and DMF) but similar to that of HMPA without the disproportionation reaction of the silane; that is:



Equation 3.4

3.4.3 Summary

The interactions of HSiX_3 ($\text{X} = \text{Cl}, \text{OTf}$) with neutral nucleophiles in solution further demonstrated the effects of steric and electronic properties of the reactants on the coordination chemistry at silicon and the possible activation of Si-H bond by pentacoordination.

Steric effects

Hexacoordination is the predominant species in every interaction of HSiX_3 ($\text{X} = \text{Cl}, \text{OTf}$) with Nu^{I} (NMI, DMAP and DMF) as a result of the effect of the small size of hydrogen with increased electron withdrawing ability relative to a methyl group. The steric hindrance of the silane is so reduced by the replacement of R (Me, Ph) by H that hexacoordination is first observed with HMPA reacting with HSiCl_3 .

However, the size of the leaving groups also contributes to the coordination at silicon as HSiX_3 always proceeds initially to increase its coordination without cleavage of the leaving groups. Therefore only pentacoordination was produced in reactions of HSiOTf_3 with Nu^{II} (HMPA and DMPU) as the triflate groups have relatively larger size than chlorine groups.

Electronic effects

The electronic effects come from the leaving groups and the nucleophile. The more electron withdrawing triflate groups accelerate the formation of the maximum coordination as they can make the coordination centre more electropositive while chlorine tends to have a smaller equilibrium constant K for the formation of the final product. A weak nucleophile also results in a smaller K as it has less ability to donate its electrons, as indicated by the formation of only pentacoordination in the reaction of HSiCl_3 with DMPU.

Decomposition of Si-H bond

The decomposition of Si-H bond was observed in the interactions of HSiCl_3 with either DMF or HMPA or DMPU and the interaction of HSiOTf_3 with HMPA to produce either H_2 (with DMF) or dihydridosilyl species (with HMPA or DMPU). Presumably this reaction takes place by a pentacoordinated intermediate, through which the Si-H bond is activated. The exact mechanism is an interesting subject which remains to be studied.

3.5 Reactivity of trifunctional silanes RSiX_3 ($\text{R} = \text{Me, Ph, H}$; $\text{X} = \text{O-}i\text{Pr, Cl, OTf}$) towards nucleophiles

The reactivity of a silane is always related to the numbers of functional groups, and the nature of the R and X groups. The coordination chemistry of trifunctional silanes with a single nucleophile is demonstrated as above. The relative reactivities of RSiX_3 ($\text{R} = \text{Me, Ph, H}$; $\text{X} = \text{O-}i\text{Pr, Cl, OTf}$) towards nucleophiles are to be discussed in this subsection, involving mostly a competitive reaction system with two or more silanes and one nucleophile.

$\text{HSi(O-}i\text{Pr)}_3 + \text{NMI}$

The reactivity of trifunctional silanes is heavily dependent on the leaving groups.

While reacting with HSiOTf_3 highly exothermically, NMI hardly reacts with $\text{HSi}(\text{O-}i\text{Pr})_3$ even with high proportions of NMI and at low temperature as shown in Table 3.23. There was little change in the ^{29}Si and ^1H NMR properties of the

Table 3.23 NMR data of the mixtures of $\text{HSi}(\text{O-}i\text{Pr})_3 + r$ NMI.

r	Temp.(K)	$\delta^{29}\text{Si}(\text{ppm})$	$J_{\text{Si-H}}(\text{Hz})$	$\delta^1\text{H}(\text{ppm})(\text{O-}i\text{Pr})$
0.0	300	-62.45	280.3	7.33; 4.32, 4.25(mt); 1.25
1.0	300	-62.40	285.8	7.31; 4.31, 4.26(mt); 1.24(d)
6.0	300	-62.56	284.3	7.27; 4.31, 4.24(mt); 1.22(d)
6.0	223	-61.61	278.3	7.28; 4.31, 4.24(mt); 1.22(d)

$c = 0.42$ mmol./ml related to the silane in CDCl_3 .

mixtures of $\text{HSi}(\text{O-}i\text{Pr})_3$ with one to six equivalents of NMI at room and low temperatures. This arises from the poor leaving ability of the leaving groups. It only forms pentacoordination with very strong nucleophiles such as $\text{HK}^{131, 132}$. The poor ability to increase coordination of $\text{HSi}(\text{O-}i\text{Pr})_3$ with nucleophiles clearly demonstrated the importance of the nature of the leaving groups towards the reactivity of silanes

$\text{MeSiCl}_3 + \text{PhSiCl}_3 + \text{HMPA}$

The competitive reaction of MeSiCl_3 with PhSiCl_3 in the presence of HMPA has shown that these two silanes have a very similar reactivity towards HMPA as the ^{29}Si chemical shifts of the corresponding silane in the mixtures moved in a parallel manner to high field with the increase in the number of equivalents of HMPA, as

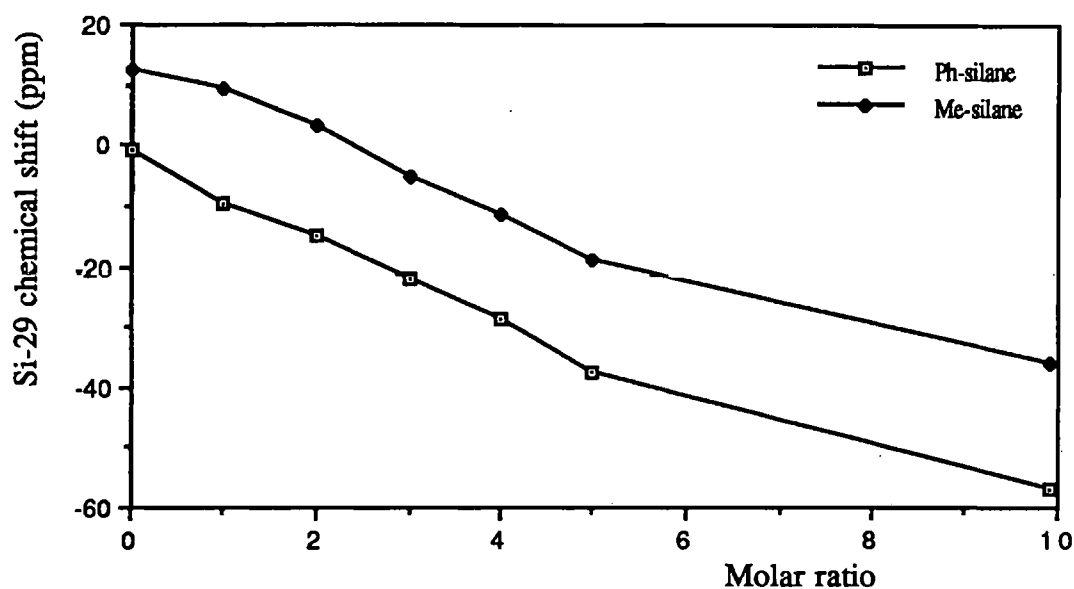


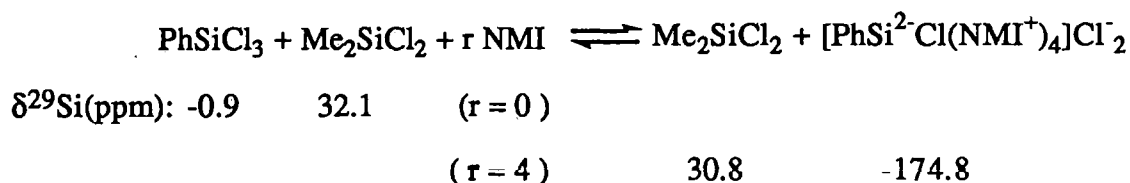
Figure 3.9 $\delta^{29}\text{Si}$ values of the mixtures of $\text{PhSiCl}_3 + \text{MeSiCl}_3 + r \text{ HMPA}$.

$c = 0.3 \text{ mmol./ml}$ related to each silane in CDCl_3 .

illustrated in Figure 3.9. Compared with the methyl group, the phenyl group is more electron withdrawing, but also has a bigger size. The balance of the steric and electronic effects leads PhSiCl_3 to have similar coordination and reactivity to MeSiCl_3 .

$\text{PhSiCl}_3 + \text{Me}_2\text{SiCl}_2 + \text{NMI}$

The importance of the numbers of the functional groups to the reactivity of a silane is clearly demonstrated in the competitive reactions of PhSiCl_3 with Me_2SiCl_2 in the presence of NMI as shown in Scheme 3.12. The ^{29}Si chemical shifts of the mixture

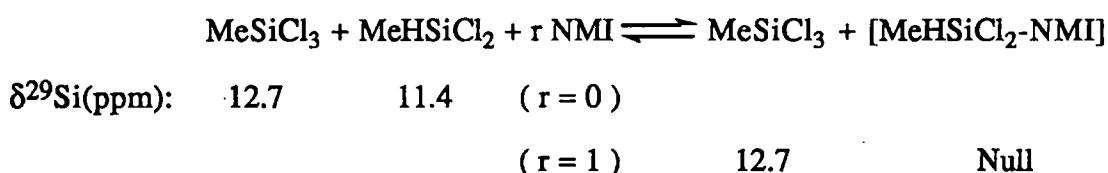


Scheme 3.12 The competitive reaction of PhSiCl_3 with Me_2SiCl_2 in CDCl_3 .

with four equivalents of NMI indicated that PhSiCl_3 formed a hexacoordinate complex (-174.8 ppm) while Me_2SiCl_2 was nearly intact (30.8 ppm). The increased reactivity in the more highly functionalized compound can be attributed to the decreased steric hindrance from R or X groups and the enhanced partial positive charge at silicon resulting from the more electronegative functional groups.

$\text{MeSiCl}_3 + \text{MeHSiCl}_2 + \text{NMI}$

The attribution of steric effect to the coordination and reactivity of a silane is of special importance. This is reflected by the enhanced reactivity towards NMI of MeHSiCl_2 compared with MeSiCl_3 as demonstrated in Scheme 3.13. The ^{29}Si



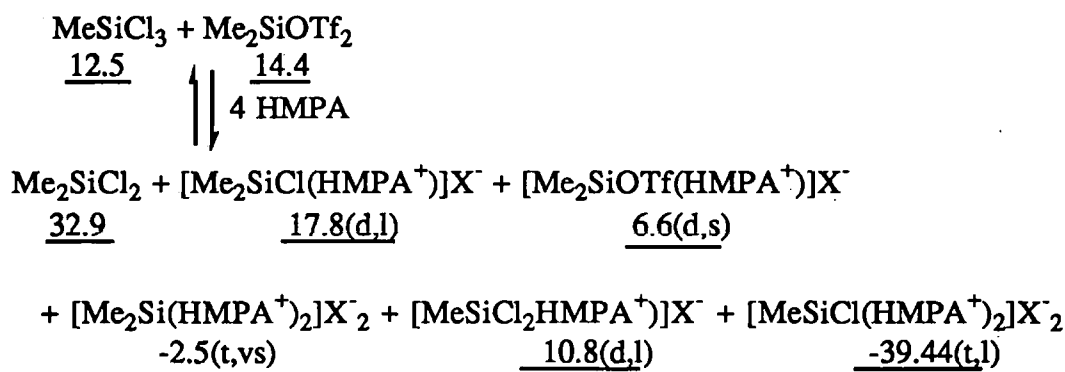
Scheme 3.13 Competitive reactions of MeSiCl_3 with MeHSiCl_2 in $\text{CD}_3\text{CN} + \text{CDCl}_3$.

chemical shift of MeSiCl_3 was not changed at all in the presence of one equivalent of NMI while the co-existing MeHSiCl_2 became null signal, which has been described as intermediate exchanges among the coordinated species. The only explanation of the enhanced reactivity of the silane by a displacement of a chlorine by a hydrogen group, *eg.* a decrease of the number of functional groups of a silane, is that Si-H bond has the least steric hindrance.

However, the reactivity of the silanes with Si-H bond is comparable individually and the more functional groups a silane has the more reactive it will be. Taking the mixture of equimolar MeHSiCl_2 and HSiCl_3 and HMPA in solution for an example, the chemical shift of HSiCl_3 moved to -51.7 ppm while that of MeHSiCl_2 remained at 12.4 ppm.



The activation of the reactivity by good leaving groups can never be overestimated. The examination of the mixtures of MeSiCl₃ and Me₂SiOTf₂ with r HMPA by ²⁹Si NMR showed that both silanes were in various substituted stages. The typical compounds with four equivalents of HMPA are presented in Scheme 3.14. It is clear



Scheme 3.14 The competitive reaction of MeSiCl₃ and Me₂SiOTf₂ in the presence of HMPA in CD₃CN + CDCl₃ solution (The figures quoted under each species are the δ²⁹Si values observed of that species).

that the silanes were redistributing functional groups and each product was reacting with HMPA except Me₂SiCl₂. The interchanges of leaving groups between the two silanes also modified the coordination and reaction pathways of the trifunctional silane as there were no ²⁹Si NMR signals observed at high field, consistent with hexacoordination, until there were at least four equivalents of HMPA (r ≥ 4) present.

Summary

Generally speaking, trifunctional silanes are more reactive than the corresponding difunctional silanes. However every group surrounding silicon will affect the reactivity and coordination of the silane by steric and electronic effects. This is so complicated a system that quantitative analysis is almost impossible with the data available. But

there must be thresholds for the steric and electronic effects according to particular patterns of reactivity and coordination of a silane, which remains to be studied in the future.

3.6 Conclusion to Chapter 3

The interactions of trifunctional silanes RSiX_3 ($\text{R} = \text{Me, Ph, H}$; $\text{X} = \text{F, Cl, OTf}$) with neutral nucleophiles in solution studied by ^{29}Si , ^1H , ^{19}F and ^{31}P NMR, conductivity measurements, and solid adducts analysis in some cases, in this chapter have shown that the coordination chemistry and reaction pathways of trifunctional silanes are more complicated than those of difunctional silanes, as penta- and hexa-coordinate as well as tetracoordinate silicon species are increasingly involved as the number of functional groups is increased by one.

The coordination at silicon is determined by the steric and electronic properties of every group involved and develops sequentially as the quantity of the nucleophiles increases. Tetra-, penta- and hexa-coordination at silicon is observed either in intermediates or as final adducts. Although it is difficult to outline comprehensive rules for the coordination and reactivity of the trifunctional silanes with the limited data, the following general conclusions can still be drawn:

(I) Trifunctional silanes RSiX_3 form adducts with nucleophiles more readily than the corresponding difunctional silanes; the increased reactivity can be attributed mainly to the enhanced electrophilicity at the silicon centre resulted from a replacement of R group by a more electronegative functional group.

(II) The maximum coordination number of a final adduct of trifunctional silane with nucleophiles is often greater by one than the that of the corresponding difunctional silane, but the highest coordination number at silicon is six; no evidence of heptacoordination was found.

(III) A replacement of the R (R = Me, Ph) group by H can increase the coordination number of the ultimate adduct with nucleophiles by one if it is less than six; take HMPA for example, it forms hexacoordinated products (188, 189) with HSiCl_3 but the silicon is pentacoordinated (162, 165, 166) with RSiX_3 (R = Me, Ph; X = Cl, OTf). This is because of a combination of the remarkably small size of H ($E_s = +1.24$), and the greater electron withdrawing effect ($\sigma^* = 0.49$).

(IV) MeSiX_3 and PhSiX_3 have similar coordination and reactivity with nucleophiles; although phenyl has a larger size ($E_s = -2.25$) than methyl ($E_s = 0.00$), it is more electron withdrawing ($\sigma^*_{\text{Ph}} = +0.75$, $\sigma^*_{\text{Me}} = 0.00$). A balance of the steric and electronic effects, therefore, leads the phenyl silanes to have similar coordination and reactivity to the corresponding methyl silanes

(V) Highly electron withdrawing and good leaving groups lead the silane to extra-coordination more easily and consequently to be more reactive; the extra-coordination and reactivity sequence is $\text{OTf} > \text{Cl} > \text{F} > \text{OR}$. For example, MeSiOTf_3 and HSiOTf_3 readily form hexacoordinate species (equivalent to 153, 154 etc), whereas with DMF and PhSiF_3 only produce pentacoordinate species (172) while $\text{HSi}(\text{O-}i\text{Pr})_3$ has no reaction at all even with NMI. This is because of the differences of the electrophilicity of the silicon centre and possibly, as Corriu proposed⁹⁵, of the stretch of the Si-X bonds.

(VI) The large size and the readiness to leave of the leaving groups also tend to restrain extracoordination; a good leaving group is always easy to be substituted. The reason that hexacoordinate species 188, 189 were observed with HSiCl_3 and HMPA and tetracoordinate species 163 was produced with MeSiOTf_3 and two equivalents of HMPA is that the triflate groups have larger size and are more ready to leave than chlorine groups.

(VII) The maximum coordination number at silicon is also controlled by the possible steric hindrance of the attacking nucleophiles upon complexation. The less sterically

hindered nucleophiles Nu^{I} , including NMI, DMAP and DMF, ultimately form adducts with trifunctional silanes with coordination number at silicon greater by one than those formed from spacially demanding nucleophiles Nu^{II} , such as HMPA and DMPU, if the number is less than six. The only exception is that HMPA formed a tetracoordinated complex (174) with PhSiF_3 , which is two less than the hexacoordination at silicon (173) produced with NMI.

(VIII) The interactions of trifunctional silane with nucleophiles proceed by coordinated intermediates, ranging from four to six; some of them are quite stable and exchange slowly. This is the result of the balance of the steric and electronic effects of both the silanes and the nucleophiles.

(IX) The coordination of the intermediates can be altered by the quantity of the nucleophile in solution. This is very important as a catalytic amount of nucleophile, which is used in most applications and mechanistic rationalizations of silicon compounds, will not alter the coordination of the intermediates at silicon significantly.

(X) Pentacoordination without substitution (152, 161, 172, 180, 183, 186) is normally produced with nucleophiles in molar ratios up to one equivalent relative to the silane, which reflects that the trifunctional silanes have the ability to stabilize extracoordination both sterically and electronically; there are, however, two exceptions that RSiCl_3 ($\text{R} = \text{Me}, \text{Ph}$) has indications of tetracoordination (143, 175) with Nu^{I} and that HSiOTf_3 only has hexacoordination with Nu^{I} .

(XI) Substitutions of the leaving groups of the trifunctional silanes are observed to proceed by intermediates of tetracoordination (143, 163, 175), pentacoordination (144, 172, 176 and all those with Nu^{II} except 163, 189, 190) and hexacoordination (146, 178, 189, 190 and all those from triflate silanes and HSiCl_3 with Nu^{I}); poor leaving groups such as F are reluctant to be substituted and PhSiF_3 was only observed to undergo one substitution, by HMPA.

(XII) Decomposition of Si-H bonds is observed in some cases by

pentacoordination; this can be a useful way to activate the Si-H bond.

Above all, the interactions of trifunctional silanes with nucleophiles are diverse and interesting. The observations of various coordination states under different conditions can serve to interpret nucleophilic reaction mechanisms of trifunctional silicon compounds with more accuracy.

Chapter 4 Interactions of nucleophiles with SiCl_4

4.1 Introduction

The coordination chemistry and reaction pathways of the interactions of acyclic difunctional and trifunctional silanes with neutral nucleophiles are heavily dependent on the number of functional groups and the nature of the R groups, the leaving groups X and the nucleophiles as stated above. Tetrafunctional silanes SiX_4 have been found to form adducts easily with organic bases. The stoichiometry of the bases of the adducts ranged from two to six depending on the nature of the leaving groups and the nucleophiles^{58, 151}. The structures of hexacoordinated compounds such as complexes **11**⁵⁵, **12**⁵⁷ and **13**⁵⁷ were even identified by X-ray analysis. Pentacoordination^{60b, 130} is also proposed with those involving very poor leaving groups such as Si(OR)_5^- and HSi(OR)_4^- .

However, little is known about the reaction process of tetrafunctional silanes with neutral nucleophiles in solution and the steric effect on the coordination is hardly mentioned. It is the aim of this chapter to provide some information on the electronic

and steric effects on coordination at silicon of tetrafunctional silane reacting with neutral nucleophiles.

SiCl_4 was selected to represent tetrafunctional silanes. NMR spectroscopy and conductivity studies, elemental analysis of solid adducts in some cases, were the main methods to monitor the interactions of SiCl_4 with neutral nucleophiles.

4.2 The interactions of SiCl_4 with nucleophiles

Titration of SiCl_4 with nucleophiles such as NMI, DMAP, DMF, HMPA and DMPU against ^{29}Si and ^1H NMR chemical shifts and conductivity in solution were performed as with di- and tri-functional silanes. The following discussions develop, not according to the nucleophilicity, but according to the possible steric hindrance of the nucleophiles upon complexation.

$\text{SiCl}_4 + \text{NMI}$

A solid adduct was very easy to form with the addition of NMI into SiCl_4 solution, even in a solvent mixture of CD_3CN and CDCl_3 . The NMR data of the titration of SiCl_4 with NMI are collected mostly in the presence of solids as shown in Table 4.1. The high field shift of ^{29}Si to about -191 ppm when $r \geq 2$ clearly demonstrated the formation of hexacoordinate complex. This complex is most likely to have three equivalents of NMI associated to silicon with one substitution of chlorine, which is quite stable, as the ^{29}Si resonance signal co-existed with that of SiCl_4 (about -18 ppm) with two equivalents of NMI and became the only signal with four equivalents of NMI. The other signal at -193.45 ppm with three equivalents of NMI probably came from a hexacoordination without substitution. The deshielded proton signals of NMI suggested that the formation of complexes involving NMI proceeded mainly when $r \leq 3$, though the signals were split because of the inhomogeneity of the solution. The solid adduct separated with extra NMI present was found by elemental analysis to have the formula of $\text{SiCl}_4 \cdot 3 \text{ NMI}$.

Table 4.1 NMR data of the mixtures of $\text{SiCl}_4 + r \text{ NMI}$.

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)
0.0	-18.65	(7.37, 6.96, 6.85, 3.53)
1.0	-18.76, Null	9.04(s), 8.69; 7.45, 7.36; 7.25, 7.18; 4.01(s), 3.92
2.0	-18.87, -191.36	8.95, 8.65(s); 7.40, 7.38, 7.18(s,br); 3.98, 3.90(s)
3.0	-191.25, -193.45	9.41(s), 8.72; 7.71(s), 7.41(br), 7.17(s); 4.10(s), 3.93
4.0	-191.25	8.81; 7.53, 7.18; 3.98
4.8	-191.23	8.80; 7.36; 7.18; 3.96
6.8	-191.23	8.87; 7.61, 7.34; 7.16, 7.00; 3.90(s), 3.70

c = 0.4 mmol./ml related to the silane in $\text{CD}_3\text{CN} + \text{CDCl}_3$ with solids present except

r = 0.0, 4.0 and 4.8 where no solid existed.

$\text{SiCl}_4 + \text{DMAP}$

Solids were so readily deposited from the SiCl_4 / DMAP mixture that the titrations were impossible to perform. However a ^{29}Si resonance signal at -163.0 ppm was observed with seven equivalents of DMAP and solids in a mixture solvent of CD_3CN and CDCl_3 (c = 0.07 mmol./ml related to the silane), which suggests the formation of hexacoordination as well. However, the solid isolated from the mixture was found by elemental analysis to have only two equivalents of DMAP associated to silicon; that is $\text{SiCl}_4 \cdot 2 \text{ DMAP}$. Therefore there is probably no substitution but association reactions in the interaction of SiCl_4 with DMAP.

SiCl₄ + DMF

The addition of DMF into SiCl₄ produced hexacoordination immediately as shown by the NMR data as presented in Table 4.2. However there were two ²⁹Si resonance signals in the range of hexacoordinate silicon with equivalents of DMF from one to six, though the one of about -181.3 ppm switched to the one of -184.8 ppm progressively after three equivalents of DMF were added and became the only resonance with 7.5 equivalents of DMF. There were at least two sets of proton signals as well. Therefore there must be two kind of hexacoordinated complexes. Like the case of

Table 4.2 NMR data of the mixtures of SiCl₄ + r DMF in CDCl₃.

r	δ ²⁹ Si (ppm)	δ ¹ H (ppm)
1.0	-19.02(65%) -181.27(28%) -184.81(7%)	9.02, 8.89; 3.53, 3.30, 3.29(70%) 8.62, 3.46, 3.24(30%)
2.0	-19.02(40%) -181.27(35%) -184.89(25%)	9.01, 8.92; 3.54, 3.31, 3.30(60%) 8.63; 3.49, 3.25(40%)
3.0	-181.35(55%) -184.89(45%)	9.00, 8.92; 3.56, 3.31(60%) 8.63; 3.50, 3.25(40%)
4.2	-181.27(40%) -184.81(60%)	9.00, 8.94; 3.57, 3.31(60%) 8.64; 3.52, 3.25(40%)
6.0	-181.35(10%) -184.81(90%)	9.00; 8.69(s); 3.57, 3.32, 3.26(s) (sbr, 60%) 8.17; 3.08, 2.91(40%)
7.5	-184.73(100%)	9.03; 3.58, 3.32(sbr, 40%) 8.16; 3.07, 2.90(60%)

c = 0.5 mmol./ml related to the silane.

NMI with SiCl_4 , the two hexacoordinate species can correspond to a direct association of two equivalents of DMF to form a neutral six-coordinate adduct and followed by one substitution of chlorine by DMF to produce an ionic hexacoordination.

Conductivity studies of SiCl_4 + NMI (or DMF)

Titration of SiCl_4 with NMI in solution against the conductivity of the mixtures suggest that ions were not produced until the NMI was present at a ratio of more than two equivalents in the mixtures of SiCl_4 with NMI. With DMF the titration shows that there was no significant free ionic species in the mixtures of SiCl_4 with any equivalents of DMF as shown by the titration curves in Figure 4.1. This means that

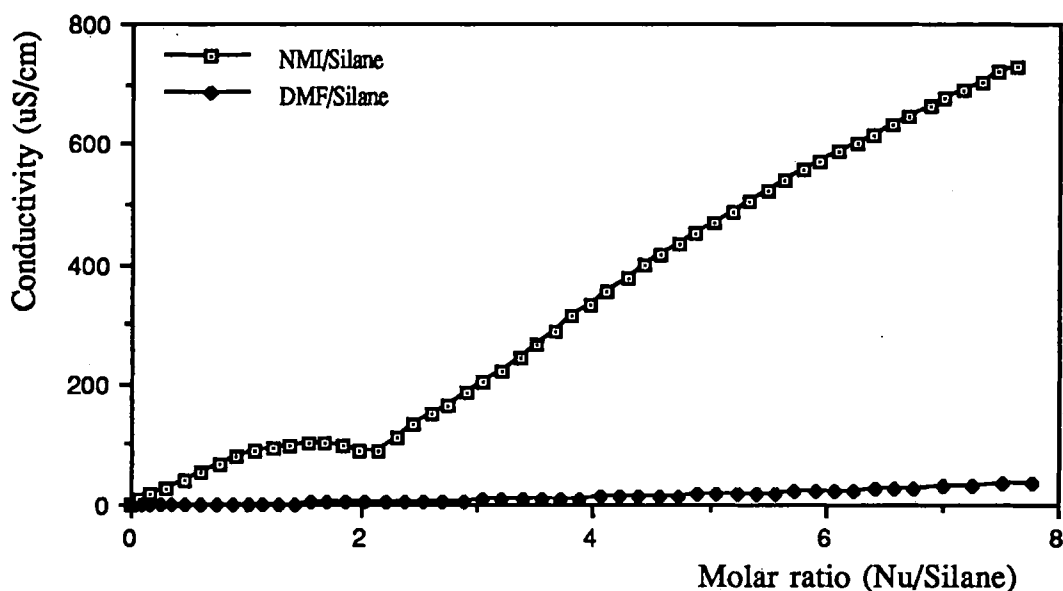
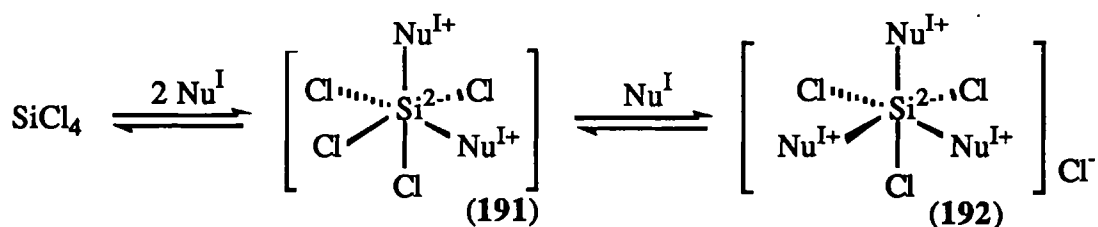


Figure 4.1 Conductivity titrations of SiCl_4 with NMI or DMF.

$c = 0.1 \text{ mmol./ml}$ related to the silane in $\text{CH}_3\text{CN} + \text{CHCl}_3$ for the titration with NMI and in CHCl_3 for the titration with DMF.

the substitution of chlorine by NMI happened after hexacoordination formed and there was only one substitution as the conductivity reading is relatively low. In the case of DMF, there was less significant substitution even considering the possible tight ion pair in a non polar solvent CHCl_3 .

Therefore the interactions of SiCl_4 with Nu^{I} (NMI, DMAP and DMF) can be expressed in Scheme 4.1. Hexacoordination **191** resulted from direct association of



Scheme 4.1 Summary of the interactions of SiCl_4 with Nu^{I} .

two equivalents of nucleophiles. For NMI and DMF substitution product **192** is preferred with an excess of the nucleophile whereas for DMAP solid **191** deposited before any significant substitution took place.

SiCl_4 + HMPA

By contrast to the easy formation of hexacoordination of Nu^{I} with SiCl_4 , a slow coordination process was observed by NMR spectroscopy with the spacially demanding nucleophiles, such as HMPA and DMPU, reacting with SiCl_4 .

The additions of HMPA in to SiCl_4 solution resulted in a null signal of silicon-29 resonance up to five equivalents of the nucleophile as shown in Table 4.3. The signal at -205 ppm, appeared with seven equivalents of HMPA and became natural width with eight equivalents of HMPA, and indicated the final formation of a stable hexacoordinate silicon complex. The deshielded sharp proton signals of HMPA suggested that some HMPA was involved in complexation and was in fast exchange with those of free HMPA. The resonance signals of ^{31}P were broadened and initially shifted to high field to about 17 ppm, which is the first observation of increases of shielding of HMPA upon complexation, followed by low field movement to around 25 ppm. All these arise from the steric effect, *eg.* the large size and the steric hindrance of HMPA. The crowded molecule upon complexation of HMPA has high energy profile,

Table 4.3 NMR data of the mixtures of $\text{SiCl}_4 + r \text{ HMPA}$ in CDCl_3 .

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^{31}\text{P}$ (ppm)	$\delta^1\text{H}$ (ppm)
0.0	-18.92	(23.89)	(2.68, 2.59)
1.0	Null	20.06(sbr)	2.83, 2.71
2.0	Null	19.65(br)	2.84, 2.72
3.0	Null	17.88(vbr)	2.83, 2.72
4.0	Null	25.34, 17.30(br)	2.81, 2.70
5.0	Null	25.64(l,br), 16.73(s,br)	2.80, 2.69
7.0	-205.22(sbr)	24.84(l,sbr), 16.42(vs,br)	2.76, 2.66
8.0	-205.47(sh)	24.53(l), 16.19(vs,vbr)	2.75, 2.64

c = 0.4 mmol./ml related to the silane.

by which fast exchanges and substitutions are more ready to take place.

$\text{SiCl}_4 + \text{DMPU}$

Examinations of the interaction of DMPU with SiCl_4 by ^{29}Si NMR present a good example of a spacially demanding nucleophile being reluctant to increase coordination at silicon. Although DMPU is a weak nucleophile, it is still a little stronger than DMF, which formed hexacoordination with SiCl_4 instantly. However, the additions of DMPU into SiCl_4 solution only made the ^{29}Si resonance of the mixtures shift slowly to a high field well below the range of hexacoordinate silicon even with ten equivalents of the nucleophile, as shown in Table 4.4. Although the nature of the progressively

Table 4.4 NMR data of the mixtures of $\text{SiCl}_4 + r$ DMPU in CDCl_3 .

r	$\delta^{29}\text{Si}$ (ppm)	$\delta^1\text{H}$ (ppm)
1.0	-19.10	3.27(t), 2.94, 1.98(qu)
2.0	-20.00	3.27(t), 2.93, 1.99(qu)
3.0	-22.00	3.28(t), 2.93, 1.99(qu)
4.0	-26.10(sbr)	3.29(t), 2.93, 1.99(qu)
5.0	-32.98(sbr)	3.30(t), 2.92, 1.99(qu)
6.0	-43.71((sbr)	3.31(t), 2.92, 1.99(qu)
7.0	-54.62(br)	3.31(t), 2.92, 1.99(qu)
8.0	-66.68(br)	3.31(t), 2.92, 1.99(qu)
10.0	-82.03(vbr)	3.31(t), 2.90, 1.99(qu)
10.0	Null (at 223 K)	nr (at 223 K)

$c = 0.5$ mmol./ml related to the silane.

broadened ^{29}Si NMR signal of the mixture with the gradual increases of the equivalents of DMPU and the null signal at low temperature ($r = 10$ at 223 K) may indicate hexacoordination was involved in the exchange as well, the difficulty of DMPU to form stable extracoordinated complex with SiCl_4 is clearly demonstrated. The only reasons for the reluctance to increase coordination are the steric effect of DMPU, the crowded donor and the steric hindrance, besides the relatively low nucleophilicity of DMPU.

Conductivity studies of SiCl_4 + HMPA (or DMPU)

Conductivity titrations of SiCl_4 with nucleophiles in CHCl_3 solution have shown that a significant amount of ions were produced in the mixtures of SiCl_4 with HMPA and only a limited quantity ionic species were formed in the mixtures of SiCl_4 with DMPU as illustrated in Figure 4.2. It is conceivable that HMPA and DMPU have similar

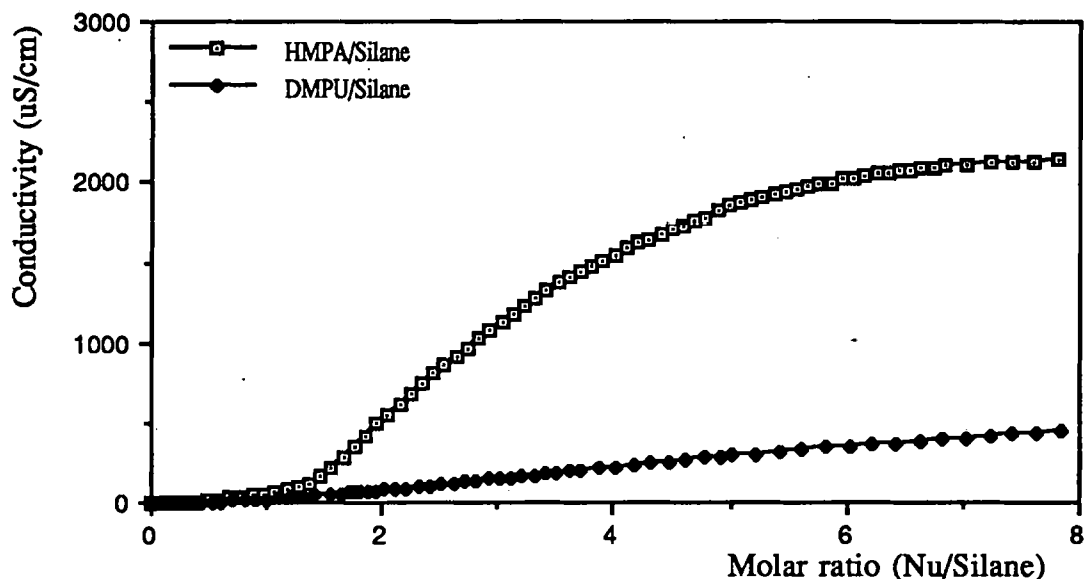
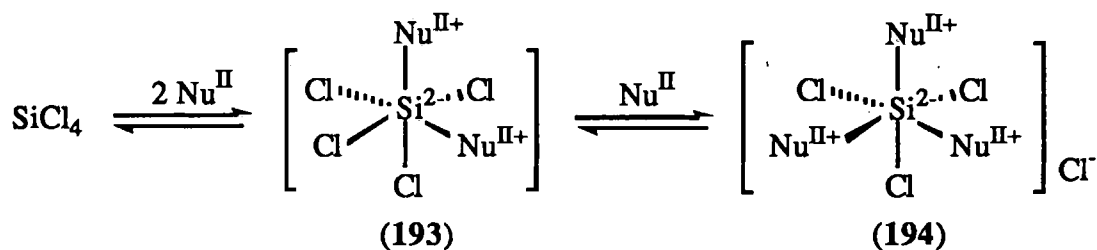


Figure 4.2 Conductivity titrations of SiCl_4 with HMPA or DMPU in CHCl_3 .

$c = 0.19$ and 0.13 mmol./ml related to the silane for the titrations with NMI and DMPU respectively.

reaction pathways with SiCl_4 . Both initially form hexacoordinated complexes with SiCl_4 , where a substitution takes place. As DMPU is a much weaker nucleophile and only has a small amount of hexacoordinated complexes in equilibrium, it is reasonable that much fewer ions are produced than in the case with HMPA. Considering that the complexes are so crowded and that less sterically hindered NMI only results in one replacement of chlorine from SiCl_4 , it is rational that HMPA only has one substitution as well. Therefore the interactions of SiCl_4 with spacially demanding nucleophiles Nu^{II} (HMPA and DMPU) can be expressed in Scheme 4.2, similar to those of Nu^{I} .



Scheme 4.2 Summary of the interactions of SiCl₄ with Nu^{II} (HMPA, DMPU)

4.3 Summary

The NMR and conductivity studies of the interactions of SiCl₄ with neutral nucleophiles (NMI, DMAP, DMF, HMPA and DMPU) in solution have shown that hexacoordination at silicon was always produced due to the enhanced electrophilicity of the silicon centre by the four electronegative chlorine atoms and the limited steric hindrance of the small size of the functional groups. No evidence of pentacoordination was found.

Substitution of chlorine by way of hexacoordination is limited to one, probably because of the poor leaving ability of the chlorine group.

The reactivity of tetrafunctional silane is very much dependent on the functional groups sterically and electronically. For example, Si(OEt)₄ has no reaction with NMI. The ²⁹Si resonance signal at -81.7 ppm was unchanged even with six equivalents of NMI and at 220 K (c = 0.75 mmol./ml in CDCl₃).

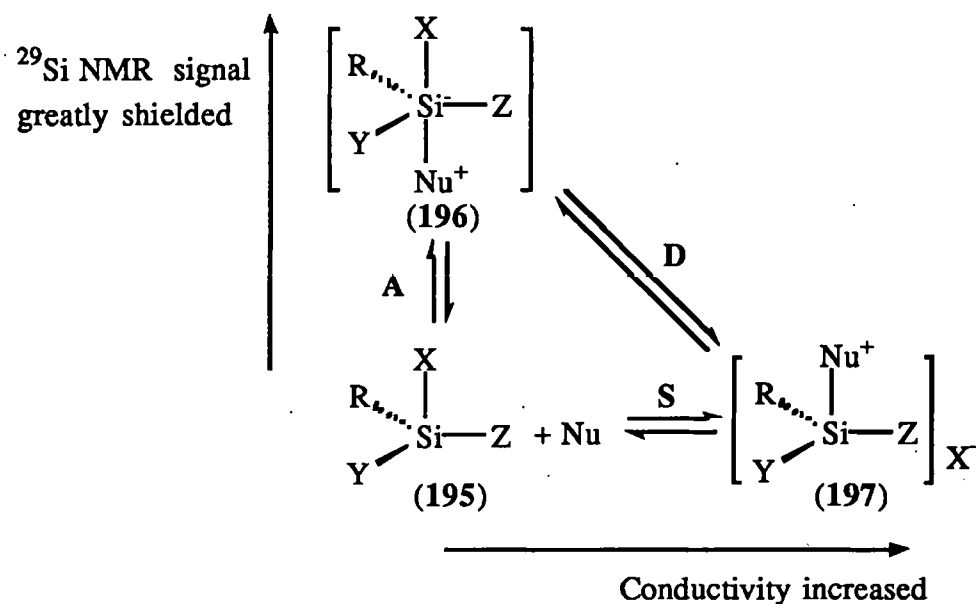
The steric effect of a nucleophile is more important than its nucleophilicity in formation of hexacoordination with SiCl₄. Less steric hindered nucleophiles Nu^I including NMI, DMAP and DMF form hexacoordination much more readily than spatially demanding nucleophiles Nu^{II} such as HMPA and DMPU. The complexes formed by Nu^{II} are more labile probably because the higher energy of the more crowded molecules.

Chapter 5 Coordination chemistry of silicon

——Summary of Chapter two to four

General

The interactions of functional silanes RSiXYZ (R = alkyl, aryl, H; X = functional group, Y , Z = either R or X) with neutral nucleophiles Nu can have two possible results, which have long been in dispute as shown in Scheme 5.1. The attacking nucleophile can either directly associate with the silicon of the silane **195** (Process A) to give an extracoordinated species **196**, or simply substitute X (Process S) to produce a tetracoordinated adduct **197**. The compound **197** can also be prepared from **196** by a dissociation process D. These processes involving the interactions of multifunctional silanes $\text{R}_n\text{SiX}_{4-n}$ (R = Me, Ph, H hereinafter unless specified; X = OR, F, Cl, Br, I, OTf; n = 0, 1, 2) with neutral nucleophiles (Nu = NMI, DMAP, DMF, HMPA, DMPU) in solution were successfully monitored by NMR spectroscopy, namely the ^{29}Si resonance signals, and by conductivity measurements. Process A results in significantly shielded ^{29}Si NMR signals and process S remarkably increases the conductivity of the solution. A good deal of information concerning coordination chemistry of silicon as well as the reaction pathways has been obtained. Four-, five-



Scheme 5.1 Nucleophilic reaction profile of functional silanes.

and six-coordinated silicon has been observed in the interactions of multifunctional silanes with neutral nucleophiles in solution. Some of the solid adducts have been examined by elemental analysis as well as NMR spectroscopy. Each of the complexes, most of which provide the first direct experimental evidence for such species as penta- and hexa-coordinated complexes of simple acyclic silanes, can serve as models for intermediates in the nucleophilic reactions of organosilicon compounds.

The coordination at silicon depends on a balance between the electronic and steric effects of all the surrounding groups including the attacking nucleophiles. The electronic effect comes from the electron density and distribution around silicon, including the electron withdrawing ability of all the groups, such as electronegativity and leaving ability of the functional groups, and the donicity of the nucleophiles. The steric effect arises from the mutual exclusion among the crowded surrounding groups due to the increase of coordination and the size of the groups involved. Generally speaking, the steric effect is more important than the electronic effect in determining the most stable coordination state as long as the reaction centre, silicon, is electrophilic. For example, the maximum coordination number of the silane-nucleophile

adducts is five for R'_2SiX_2 and is six for $R'HSiX_2$ ($R' = Me, Ph$ hereinafter unless specified); the smaller sized and lower donicity nucleophile NMI reacting with silanes always has a greater coordination at least by one than the spacially demanding but higher donicity nucleophile HMPA when the coordination of the HMPA complex is four or five in the ultimate adducts. No evidence of heptacoordination at silicon was found.

It is most likely that there are electronic and steric thresholds in formation of extracoordinate silicon. Although the exact requirements are difficult to define with the limited data, the specific electronic and steric effects in production of tetra-, penta- and hexa-coordinate silicon observed in the interactions of functional silanes with nucleophiles can be summarized according to the numbers of the functional groups, the nature of the R groups and the leaving groups, the nature and the quantity of the nucleophiles and the reaction conditions.

The number of functional groups

The coordination at silicon is firstly related to the numbers of the functional groups of the silane. For the $R'_{4-n}SiX_n$ ($n = 1, 2, 3, 4$) series the maximum coordination numbers with neutral nucleophiles is normally four when $n = 1$, five when $n = 2$ and six when $n = 3$ or 4, *eg.* there is a sequence of coordination ability: SiX_4 (hexa-), $R'SiX_3$ (hexa-) > R'_2SiX_2 (penta-) > R'_3SiX (tetra-).

The increased coordination ability, often together with an enhanced reactivity, with the increase in the number of electronegative functional groups X is because the silicon becomes more electrophilic and the steric hindrance is reduced by the smaller size of the X group. The electronic requirement of the formation of pentacoordination is usually easy to fulfil as the electronegativity of silicon is quite low. Consequently the restraint on the increase of coordination comes from the steric hindrance and the readiness of the leaving groups to leave. The reason that $Me_3Si(CN)_2^-$ is easily observed¹⁴⁹ is that CN^- has only a limited size and that $Me_3SiF_3^{2-}$ needs severe conditions³⁸ is that the molecule is so crowded in addition to the lack of stretch of the Si-F bonds. Although there is a negative charge intuitively located at silicon in a

pentacoordinated complex, the electrons may actually be distributed around the surrounding groups as is described by models such as "hypervalent bonding"³⁵. Therefore it is neither so difficult to meet the electronic requirement for hexacoordination when there are more electronegative groups (than silicon) bonded to silicon.

It is interesting to notice that the initial tendency of process S is reduced as the coordination ability (process A) is enhanced by the increase in the number of functional groups. For example, a substitution reaction is the predominant process for the interactions of mono-^{5, 6, 51} and di-functional silanes $R'_{4-n}SiX_n$ ($n = 1, 2$) with nucleophiles in the early stages and the association process is initially overwhelming for tetrafunctional silanes and $HSiX_3$.

The nature of the R group

The effect of the R group on the coordination at silicon is mainly due to its steric hindrance. The size of H is so small that the H-containing silanes can have a greater coordination number by one in the most stable silane-nucleophile adducts than the corresponding methyl or phenyl silanes if their coordination is under six; that is $HSiX_3$ (hexa-), $R'HSiX_2$ (hexa-), $R'SiX_3$ (hexa-) > R'_2HSiX (penta-), R'_2SiX_2 (penta-) > R'_3SiX (tetra-). The reactivity of these silanes towards nucleophiles is in a similar order. $MeHSiCl_2$ is even found to be more reactive than $MeSiCl_3$.

The electronic effect of the R groups also contributes to the coordination chemistry of silicon but with less significance. The higher electron withdrawing ability of H relative to Me (see Table 5.1) leads an additional positive effect on the H-containing silanes to increase their coordination and to enhance their reactivities. The phenyl group is also a more electron withdrawing group relative to Me. However, its much larger size than Me offsets the enhanced ability to increase coordination. Consequently phenyl silanes have nearly the same coordination chemistry as their corresponding methyl silanes. Nonetheless the nature of the increased electron withdrawing ability and the larger size of phenyl group makes the silanes and their intermediates to be slightly

Table 5.1 Taft's E_s and σ^* parameters¹⁵³.

R	E_s	σ^*
H	+1.24	+0.49
Me	0.00	0.00
Ph	-2.25	+0.75

more labile than the corresponding methyl silanes and their intermediates.

The nature of the functional groups

The functional groups affect the coordination chemistry of silicon by their electron withdrawing ability, the leaving ability and the steric hindrance including the stretching of the Si-X bonds. The ability of the functional groups to increase coordination, together with the reactivity towards nucleophiles and substitution, is in the general sequence of $I > OTf, Br \gg Cl > F \gg OR$.

In order to increase the coordination at silicon, the functional groups should firstly be electron withdrawing. The more electron withdrawing the functional groups, the easier it is for the silane to increase its coordination. For example, the silyl triflates are much more ready to form extracoordination than the corresponding chlorosilanes, though the most stable coordination is determined by the numbers of the functional groups. The lack of any significant reaction of Si-OR bonds with neutral nucleophiles is probably partially attributable to the resonance electron donating property of the OR groups or the difficulty of stretching the Si-OR bond.

The leaving ability of the functional groups is important as S is a competitive process with A as well as with process D, which results in substitution. Therefore good leaving groups tend to break away to decrease coordination at silicon. For example,

totally substituted tetracoordinated adducts are observed with $R'HSiOTf_2$ and $R'SiOTf_3$ interacting with HMPA or DMPU while the corresponding chlorosilanes maintain a pentacoordinated structure.

The relationship between the electron withdrawing ability and the leaving ability of the functional groups with respect to coordination is subtle and depends on the specific systems under examination. Take the interactions of $R'SiX_3$ ($X = Cl, OTf$) with NMI for an example, the triflates immediately form extracoordinated complexes, and the extracoordinate state is independent of the concentration of the nucleophile while the less electron-withdrawing chlorides get complicated and tetracoordinated species and even a pentacoordinated complex bridged by a chlorine atom may possibly be formed before they finally reach more stable pentacoordination with further increases of the equivalents of NMI.

The steric hindrance of the functional groups is also a factor in determining coordination at silicon. A large-sized functional group not only restrains the approach of the attacking nucleophile but also results in a crowded complex. Consequently, the large OR groups make the silanes have the least coordination reaction.

Hexacoordinate species are easily formed with $HSiCl_3$ and HMPA but not observed with $HSiOTf_3$ under similar reaction conditions. The steric effects also include the stretching of the Si-X bonds. The reluctance of $PhSiF_3$ to increase its coordination to five and six is probably due to the lack of flexibility of the Si-F bonds.

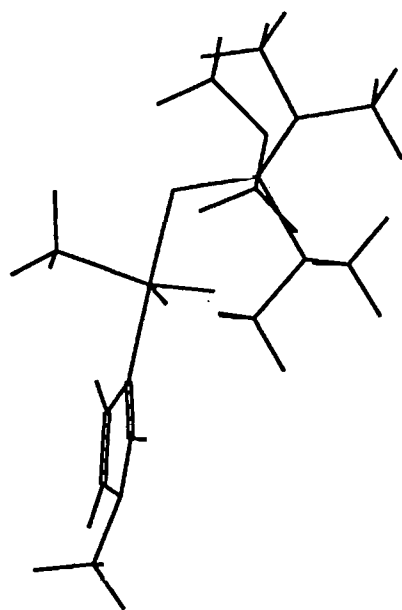
The nature of the leaving groups contributes to the reactivity of the silanes significantly, with mostly parallel effects on coordination and substitution. Groups with weak electron withdrawing and poor leaving ability and large steric hindrance reduce the reactivity of the silanes greatly. It is so reduced, in some cases, that hardly any reaction can be observed under normal conditions such as the mixtures of R'_3SiCl ⁵¹ or R'_2SiCl_2 with weak nucleophiles DMF, or DMPU at room temperature.

The nature of nucleophiles

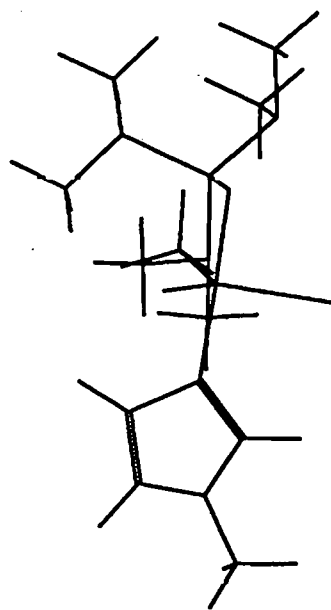
It is found that the steric parameters of the nucleophiles attribute to the coordination chemistry significantly and their donicity or nucleophilicity only affects the equilibrium constants K . The smaller the steric hindrance of the nucleophile upon complexation, the higher tendency of the silane-nucleophile adducts to increase their coordination.

The nucleophiles studied in this work can be divided into two groups according to their possible steric hindrance and their ability to extra-coordinate silicon as shown in subsection 2.2.6. The nucleophiles of smaller size and less possible steric hindrance in the first group ($\text{Nu}^{\text{I}} = \text{NMI}$, DMAP and DMF) ultimately form adducts with silanes with a greater coordination number by one than the spacially demanding nucleophiles in the second group ($\text{Nu}^{\text{II}} = \text{HMPA}$ and DMPU) within the limit of coordination; that is Nu^{II} can only form tetracoordination if Nu^{I} produces pentacoordination, and if Nu^{II} comes to pentacoordination Nu^{I} will definitely result in hexacoordination, depending on the silane under examination. There are, however, three "exceptions" due to steric effects. The first is that both Nu^{I} and Nu^{II} only form tetracoordination with $\text{R}'_3\text{SiX}$. The second is that HSiCl_3 and SiCl_4 produce hexacoordination with either nucleophile. The third is that PhSiF_3 results in hexacoordination with NMI but tetracoordination with HMPA, a coordination number difference of two.

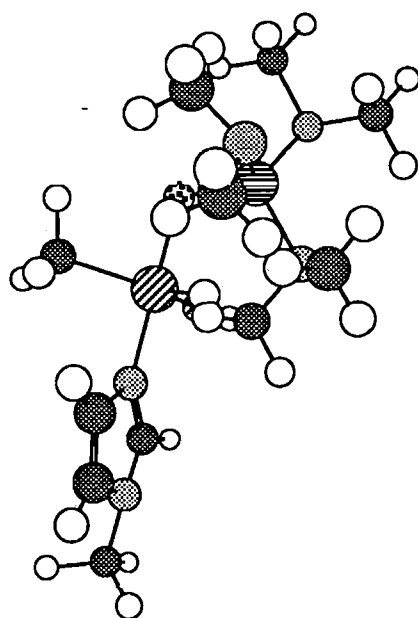
The importance of the steric effect of Nu^{I} and Nu^{II} can be further illustrated by the TBP structure of $[\text{MeHClSi}^2\text{-(NMI}^+)(\text{HMPA}^+)]$ as shown in Scheme 5.2. The HMPA bonded to silicon is not only intuitively much larger than NMI but also so crowded with the nearby groups in the trigonal plane that it greatly restrains the further attack of the coordination centre spacially. The steric hindrance of the nucleophiles in Nu^{I} is similar and so are the nucleophiles in Nu^{II} . Therefore there is no wonder that Nu^{I} forms coordination greater than Nu^{II} . It is also noticeable from the closeness between the groups in the trigonal plane, such as H, Me, Cl and the methyl groups of HMPA, that the size of the R and X groups and the flexibility of Si-X bonds of the silane are



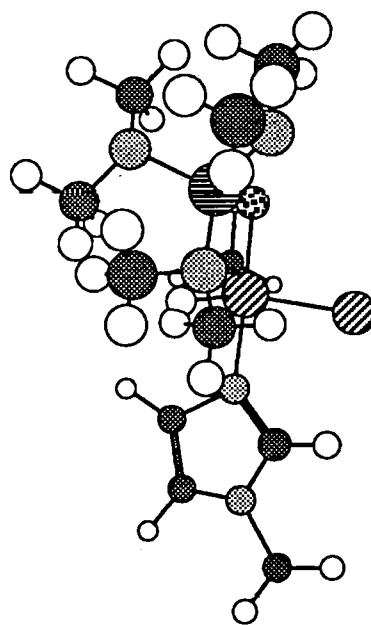
(198a)



(198b)



(198c)



(198d)

Scheme 5.2 Illustrations of the structure of $[\text{MeHClSi}^2\text{-(NMI}^+\text{)(HMPA}^+)]$.

very important, even decisive sometimes, in order to reduce the steric hindrance to suit Nu^{II} such as HMPA to bond with silicon.

A balance of the steric and electronic effects of both the nucleophile and the silane involved leads Nu^{I} and Nu^{II} to take different reaction pathways with different silanes. The nucleophilicity of the nucleophiles can not offset the particular high energy from steric hindrance. It only determines the equilibrium constant K of interactions of silanes with nucleophiles of the same category; that is stronger nucleophiles, measured by greater Taft's Beta values, have larger K : NMI , $\text{DMAP} \gg \text{DMF}$ and $\text{HMPA} \gg \text{DMPU}$. It is worth noting that the K is so small in cases of weak nucleophiles reacting with silanes with poor leaving groups that hardly any coordination reaction, or the further alteration of coordination if any, can be observed under normal conditions.

The coordination chemistry of silicon compounds is apparently not related to the nature of the donor atoms, O or N, of the nucleophiles as oxygen donor is involved in both Nu^{I} and Nu^{II} .

The steric hindrance in formation of silane-nucleophile adducts has been considered occasionally^{2, 51}. However its true importance has been revealed in this study. By taking a view of steric effects, though not defined quantitatively, the coordination chemistry of silicon and the nucleophilic reaction mechanisms of silicon compounds can be understood much better.

The quantity of the nucleophiles

The coordination at silicon in nucleophilic reactions of silanes also depends on the quantity of nucleophiles involved. A number of intermediates coordinated from four to six are observed, depended on the silane under examination and the equivalents of nucleophile present. This is extremely important in the interpretation of the nucleophilic reaction mechanisms of organosilicon compounds. On the one hand, it does demonstrate that substitution reactions of silicon compounds can take place either by tetra- or penta- or hexacoordination. On the other hand, the differently coordinated intermediates are not necessary more reactive than their parent species in

some cases.

In the presence of a small quantity of nucleophilies, often termed as catalytic amount, the intermediate varies from tetra- to penta- to hexa-coordination dependent on all the factors discussed above. For example, silanes in the series of R_3SiX (except Me_2HSiCl^{51}) and R'_2SiX_2 form tetracoordinated adducts and SiX_4 produces hexacoordination (number of functional groups); R'_2SiOTf_2 remains tetracoordinated and $R'HSiOTf_2$ becomes pentacoordinated with Nu^{II} (nature of R groups); $RHSiCl_2$ substitution and $RHSiOTf_2$ association with Nu^I (nature of leaving groups); $HSiOTf_3$ results in pentacoordination with Nu^{II} and hexacoordination with Nu^I (nature of nucleophile) etc. Although it is difficult to predict the exact coordination number of all the intermediates at this stage of the study, the steric and electronic effects are available to explain the experimental facts.

It is worth pointing out that the Si-H bonds can be activated by nucleophiles as decomposition or disproportionation reactions are observed in some interactions of H-containing silanes with nucleophiles. Presumably the activation of Si-H bonds is by a pentacoordination intermediate, though the detailed mechanism remains to be studied

The reaction conditions

As a chemical equilibrium, the coordination reaction of silicon compounds with nucleophiles in solution is inevitably affected by the reaction conditions such as temperature, concentration and the solvent.

The interactions of silanes with nucleophiles are all exothermic. A low temperature always favours the formation of more stable silane-nucleophile adducts, no matter the coordination at silicon is increased or decreased.

The coordination of nucleophiles to silicon is a process combining two species into one. Therefore high concentrations are always preferred for the production of

silane-nucleophile complexes.

The media have been proved to be very important in the study of the interactions of multifunctional silanes with nucleophiles. One of the problems is the selection of a proper solvent. Solvents with high polarity are sensitive to the silanes. For example, THF reacts with MeHSiOTf_2 violently. Non polar solvents precipitate solid adducts quite easily for lack of the ability to solvate the ionic species produced. In a few cases, the media can change the coordination process as a result from chemical equilibrium. For example, only $\text{Me}_2\text{SiCl}_2 \cdot 2 \text{ NMI}$ can be directly isolated from solution because of precipitation. More interestingly, the coordination of a silane, together with its reactivity, can be altered by exchange with a different leaving group under the catalysis of nucleophiles in the solution. For example, MeSiCl_3 forms $[\text{MeSiCl}_2(\text{HMPA}^+)]$ and $[\text{MeSi}^-\text{Cl}(\text{HMPA}^+)_2]$ progressively without extracoordinated intermediate in the presence of $\text{Me}_2\text{SiOTf}_2$, which produces substituted adducts at the same time. Again this is the impact of the steric and electronic effects from the exchanged leaving groups.

After all, the coordination chemistry of functional silanes in the nucleophilic reactions is complicated but interesting. It is a total balance of the steric and electronic effects of all species involved. The results presented in this work have hopefully shed light on the resolution of this "mystery".

Part II

Chapter 6 Reactions of Si-H containing species

6.1 Introduction

Hydrogen-containing silanes are reducing agents in the presence of catalysts²⁴. It has been suggested that the Si-H bonds were able to be activated either by transition metal complexes⁸, acids^{117, 118}, bases^{121~125} or hypercoordination^{127~132} including fluoride ion induced reactions¹⁵⁵. In the studies of coordination chemistry of silanes with nucleophiles, instances of the activation of Si-H bonds have been observed occasionally. In view of the stability of the silane-nucleophile adducts such as $[\text{Me}_2\text{Si}(\text{NMI})^+_2]$, we thought that the Si-H containing complexes such as $[\text{Me}_2\text{HSi}(\text{NMI})^+_2]$ should liberate H^- and act as reducing agents. This chapter discusses the hydrosilylation of unsaturated organic compounds such as aldehydes and ketones, by Si-H containing species, mainly those of $\text{Me}_{3-n}\text{HSiOTf}_n$ ($n = 1, 2$ in this chapter unless specified otherwise) under different conditions.

NMR spectroscopy was sensitive enough to monitor the reduction reactions of unsaturated organic compounds with Si-H containing species. The reactions were usually carried out in deuterated polar or nonpolar solvents in sealed 10 mm NMR

tubes. Therefore any reduction reactions were conveniently detected by ^{29}Si , ^{13}C and ^1H NMR spectra. Some of the products were even hydrolyzed and then checked by NMR spectroscopy.

The discussions of the reduction reactions by Si-H containing species are developed according to the reaction conditions as follows:

- (i) $\text{Me}_{3-n}\text{HSiOTf}_n + \text{R}^1\text{R}^2\text{C}=\text{O}$ ($\text{R}^1, \text{R}^2 = \text{alkyl, aryl, H}$ hereinafter unless specified otherwise);
- (ii) $\text{Me}_{3-n}\text{HSiOTf}_n / \text{Nu} + \text{R}^1\text{R}^2\text{C}=\text{O}$;
- (iii) $\text{Me}_{3-n}\text{HSiOTf}_n + \text{OTf}^- + \text{R}^1\text{R}^2\text{C}=\text{O}$;
- (iv) Miscellaneous reactions.

6.2 Reductions of $\text{R}^1\text{R}^2\text{C}=\text{O}$ with $\text{Me}_{3-n}\text{HSiOTf}_n$

Reductions of aldehydes and ketones by hydrosilylation have all been reported to require catalytic conditions^{8, 155}, probably due to the low reactivities of the silanes used. Good leaving groups such as triflate were found having an enhanced reactivity not only towards nucleophiles but also towards reduction reactions of aldehydes and ketones.

6.2.1 Reductions of aldehydes with $\text{Me}_{3-n}\text{HSiOTf}_n$

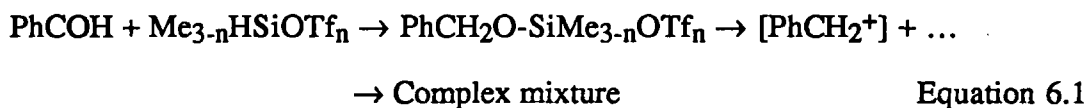
The reduction of aldehydes with H-containing methylsilyl triflates in solution (either C_6H_6 , or CHCl_3 , or CDCl_3 , or CD_3CN as solvent) was highly exothermic and was surprisingly rapid at room temperature. It was so reactive that the solution often boiled.

$\text{PhCOH} + \text{Me}_{3-n}\text{HSiOTf}_n$

The addition of PhCOH into either Me_2HSiOTf or MeHSiOTf_2 solution or vice versa always led to violent reactions and resulted in a colourless liquid phase insoluble in CDCl_3 . NMR spectra of both ^{13}C and ^1H showed that the carbonyl group of PhCOH

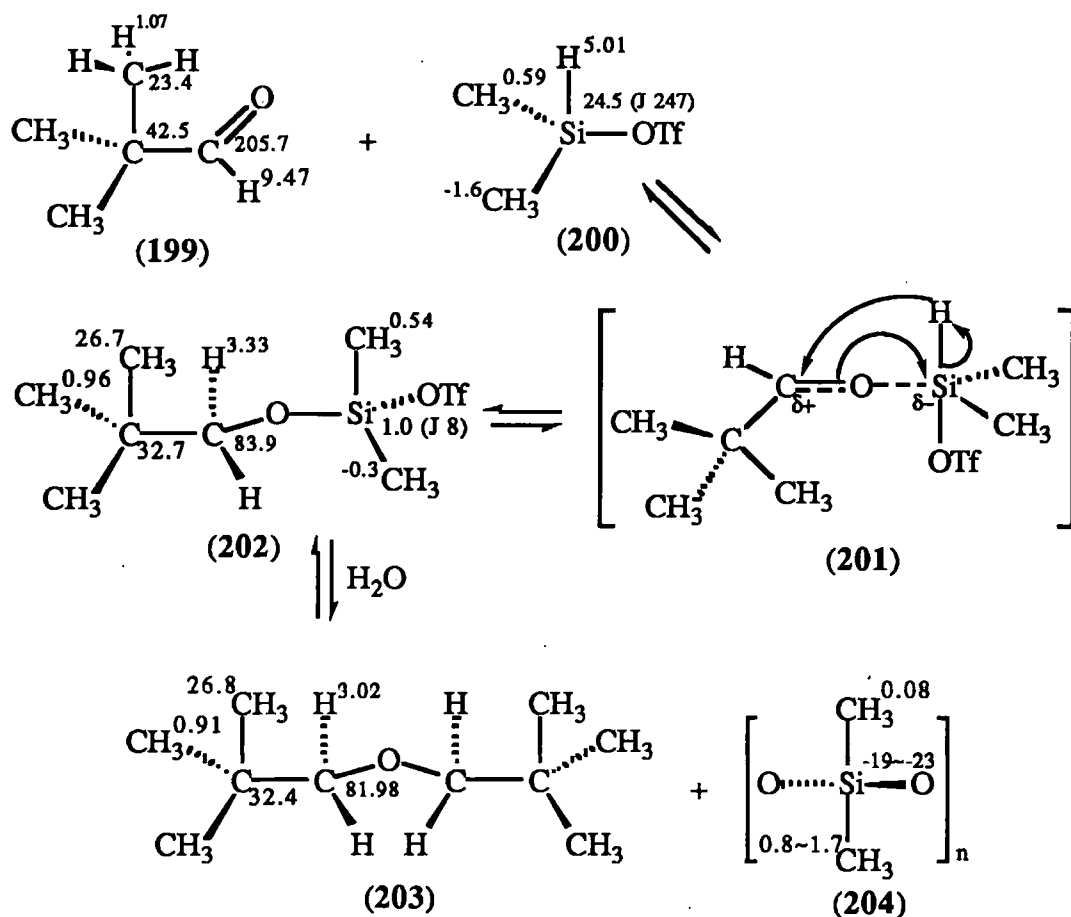
was reduced to methylene but complicated by the existence of numerous products, which is clearly indicated, for instance, by lots of CH₂ signals between 43 to 35 ppm in the ¹³C NMR spectra. These signals appeared at the very beginning and were not affected by addition of water afterwards.

However, the reaction of PhCOH with Me₂HSiOTf could be slowed down by carrying out the reaction at 0°C (ice-bath), in which case ¹³C NMR signals of CH₂ at δ 72.96 and 67.44 ppm were initially observed besides small ones between 43 to 35 ppm. Nonetheless the signals at low field disappeared after a time and the ones at high field were enhanced. Presumably a very reactive intermediate must be produced, from which a lot of products were formed . Therefore the reaction of PhCOH with Me_{3-n}HSiOTf_n can probably be described by Equation 6.1:



Me₃CCOH + Me₂HSiOTf

The products resulting from the reaction of Me₃CCOH with Me₂HSiOTf in CDCl₃ at 0°C were stable at room temperature. NMR spectra showed that the carbonyl group had been reduced as the ¹³C signal at 205.7 ppm corresponding to >C=O was replaced by a new signal at δ 83.9 ppm, which was demonstrated to be a >CH₂ group by ¹³C INEPT NMR. The Si-H coupling of the silane was decreased from 247 to 7.8 Hz simultaneously as appropriate for loss of Si-H. The possible reaction pathway and some of the ²⁹Si, ¹³C and ¹H NMR data corresponding to the species involved are illustrated in Scheme 6.1. The first step was probably the formation of a loose pentacoordinated species **201**, through which both of the Si-H bond and the carbonyl group were activated. The NMR signals of the alkoxyl moiety of **202** were exclusive and unambiguous, though those of the silane moiety were a little bit complicated. For instance, there was another ²⁹Si NMR signal at -1.8 ppm (J 7.8 Hz) together with



Scheme 6.1 Reduction of aldehyde by Me_2HSiOTf .

an additional ^{13}C signal at -0.5 ppm. However hydrolysis of **202** with NaOH and H_2O resulted in a 2,2-dimethylpropyl ether **203** and dimethylsiloxanes **204**, both of which were clearly demonstrated by their specific chemical shifts of ^{13}C , ^1H and ^{29}Si . No alcohol was found as the proton spectrum showed no signals of OH group.

Therefore there is no doubt that hydrosilyl triflates $\text{Me}_{3-n}\text{HSiOTf}_n$ can readily reduce aldehydes RCOH by hydrosilylation without any catalysis. An ether was obtained when R was a bulky alkyl group and the reduction products were complicated when R was a phenyl group.

6.2.2 Reductions of ketones with $\text{Me}_{3-n}\text{HSiOTf}_n$

The reductions of ketones $\text{R}^1\text{R}^2\text{CO}$ by $\text{Me}_{3-n}\text{HSiOTf}_n$ were similar to those of aldehydes. The reactions were also swift and exothermic and had to be carried out in

an ice-bath. NMR studies showed that the carbonyl group was reduced. However the products were very much dependent of the R¹ and R² groups as well as the conditions of hydrolysis.

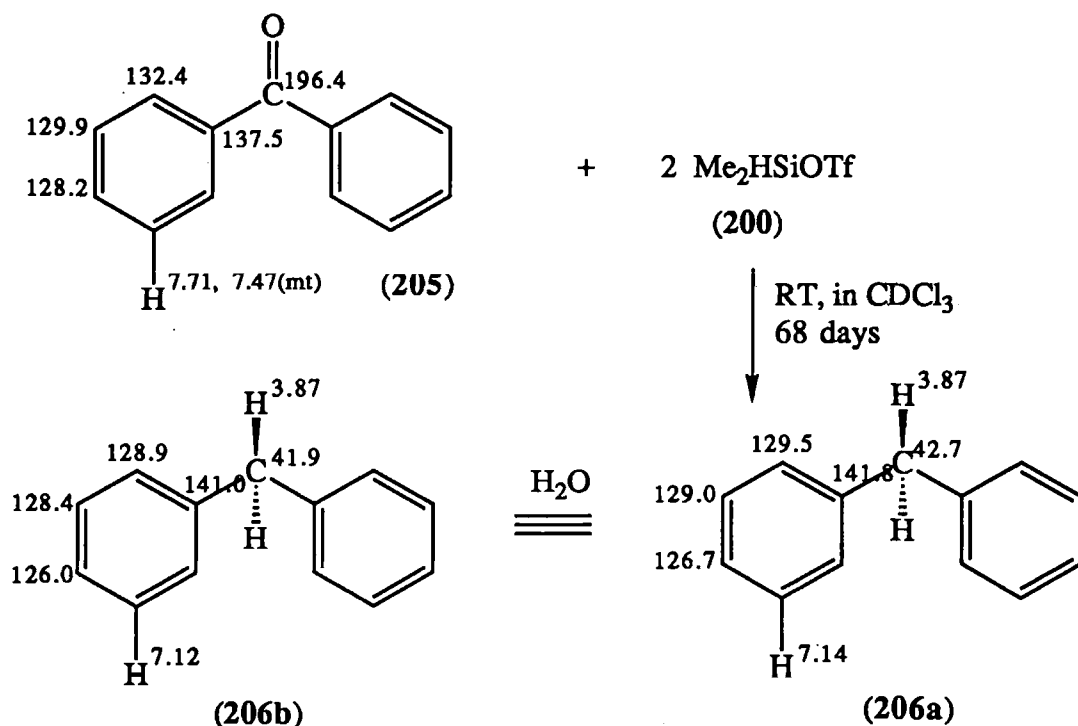
PhCOMe + Me_{3-n}HSiOTf_n

Similarly to the results of benzaldehyde, PhCOMe reacting with Me_{3-n}HSiOTf_n at room temperature produced a number of products and was even more complicated. The carbonyl group was not only reduced by MeHSiOTf₂ and Me₂HSiOTf to R₃CH, indicated by the multiplets at 42.9~37.3 and 44 ppm in the ¹³C NMR spectra but also resulted in >CH₂ compounds marked by multiplets at 49~44 and 29 ppm respectively (see Table 7.3). In addition, a small amount of the carbonyl group remained un-reduced but complexed as a number of ¹³C NMR signals around 200 ppm were also observed. These results suggest that ketones, on the one hand, were a little bit more difficult to be reduced than aldehydes but, on the other hand, they could be possibly reduced to alkanes, though the reaction of PhCOMe with Me_{3-n}HSiOTf_n at room temperature was out of control as presented in Equation 6.2.



Ph₂CO + Me₂HSiOTf

The reduction of Ph₂CO by Me₂HSiOTf in solution into Ph₂CH₂ was slow but decisive at room temperature. Some of the typical chemical shifts of ¹³C and ¹H NMR of Ph₂CO and Ph₂CH₂ in the reacting mixture was illustrated in Scheme 6.2. No intermediate was found as these NMR resonance signals were the only ones besides those of the silane. Ph₂CH₂ was directly produced as was demonstrated by ¹³C INEPT and hydrolysis, which made virtually no difference of the NMR properties between **206a** and **206b**. These results are comparable with those of ionic hydrogenation reported by Kursanov¹¹⁷ and West¹¹⁸.

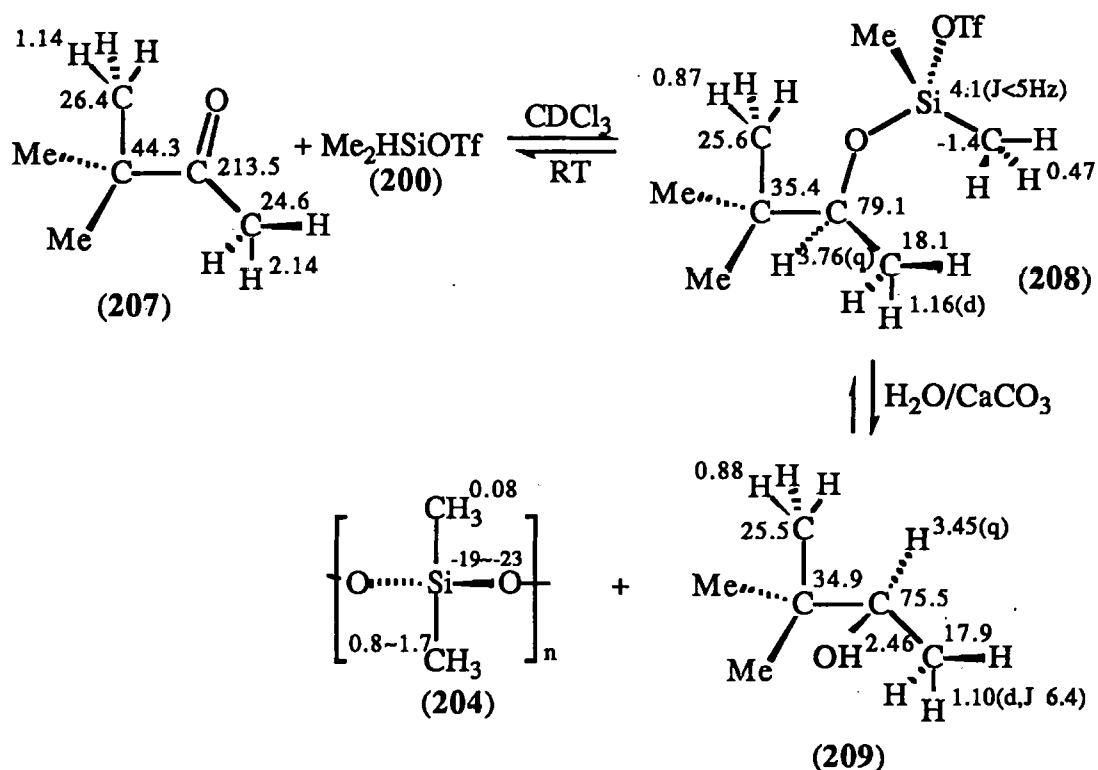


Scheme 6.2 Reduction of Ph_2CO by Me_2HSiOTf in CDCl_3 .

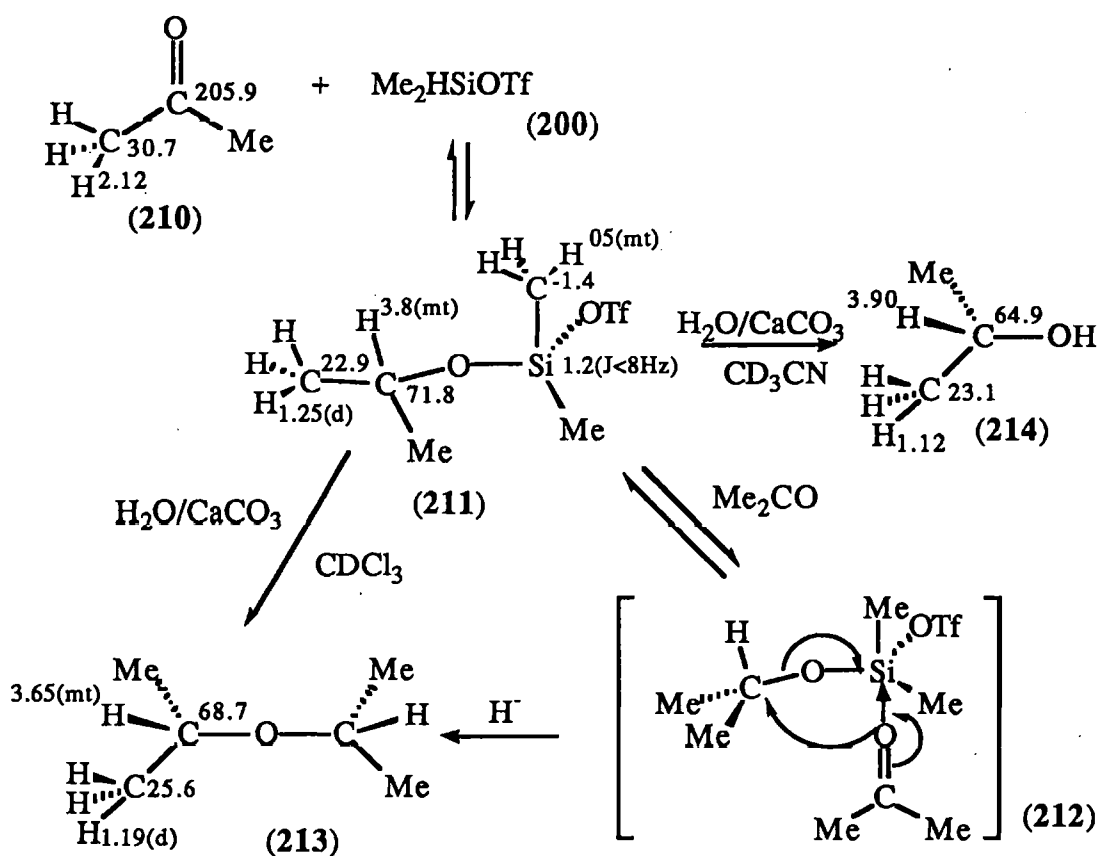
$\text{R}^1\text{COMe} + \text{Me}_2\text{HSiOTf}$ ($\text{R}^1 = t\text{Bu, Me}$)

Ketones without phenyl groups bonded to the carbonyl group were reduced by Me_2HSiOTf rapidly into alkoxy compounds even at 0°C . The mixing of Me_3CCOMe and Me_2HSiOTf in CDCl_3 resulted in a highly exothermic reaction and produced alcohol after hydrolysis as illustrated in Scheme 6.3. The exclusive and unambiguous change of chemical shifts of ^{13}C , ^1H and ^{29}Si NMR of the mixture suggested that an intermediate **208** was formed before hydrolysis to produce the alcohol **209**, which matches the reported NMR data perfectly.

Similarly, MeCOMe was reduced by Me_2HSiOTf to give an alkoxy silane species but produced an ether in addition to an alcohol as shown in Scheme 6.4. According to the changes of the chemical shifts of the signals of ^{13}C , ^1H and ^{29}Si NMR, an intermediate **211**, similar to **202** and **208**, was initially produced. However, signals also appeared simultaneously corresponding to the ether **213**, (about ten percent in CDCl_3 and forty percent in CD_3CN), which was probably by way of the complex **212**. It is also



Scheme 6.3 Reduction of Me_3CCOMe by Me_2HSiOTf .

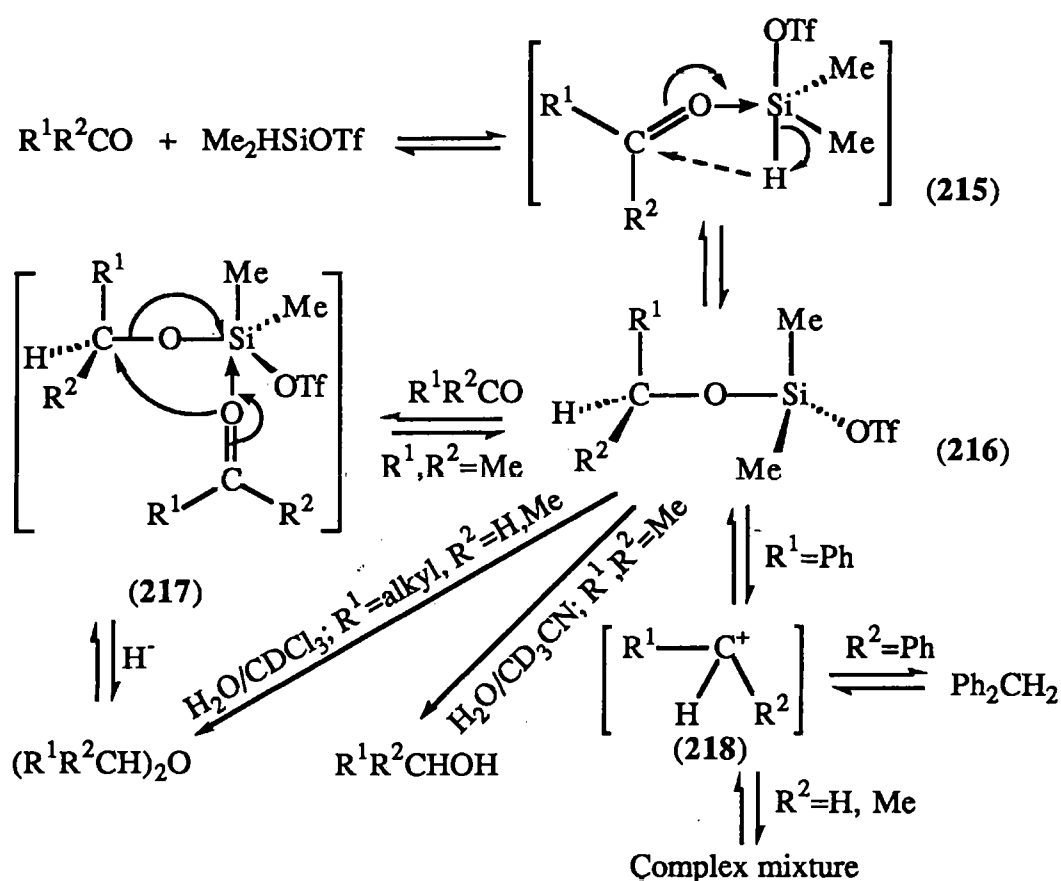


Scheme 6.4 Reduction of acetone by Me_2HSiOTf in solution.

interesting to observe that hydrolysis of **211** produced ether **213** in CDCl_3 and alcohol **214** in CD_3CN , which most likely resulted from the homogeneity of the mixtures with water.

6.2.3 Summary

In contrast to MeHSiCl_2 and HSiCl_3 , $\text{Me}_{3-n}\text{HSiOTf}_n$ is reactive enough to reduce aldehydes and ketones in solution without any catalyst, though the mechanisms may be different. The reduction of $\text{R}^1\text{R}^2\text{CO}$ by Me_2HSiOTf was summarized in Scheme 6.5.



Scheme 6.5 Summary of the reduction of $\text{R}^1\text{R}^2\text{CO}$ by Me_2HSiOTf .

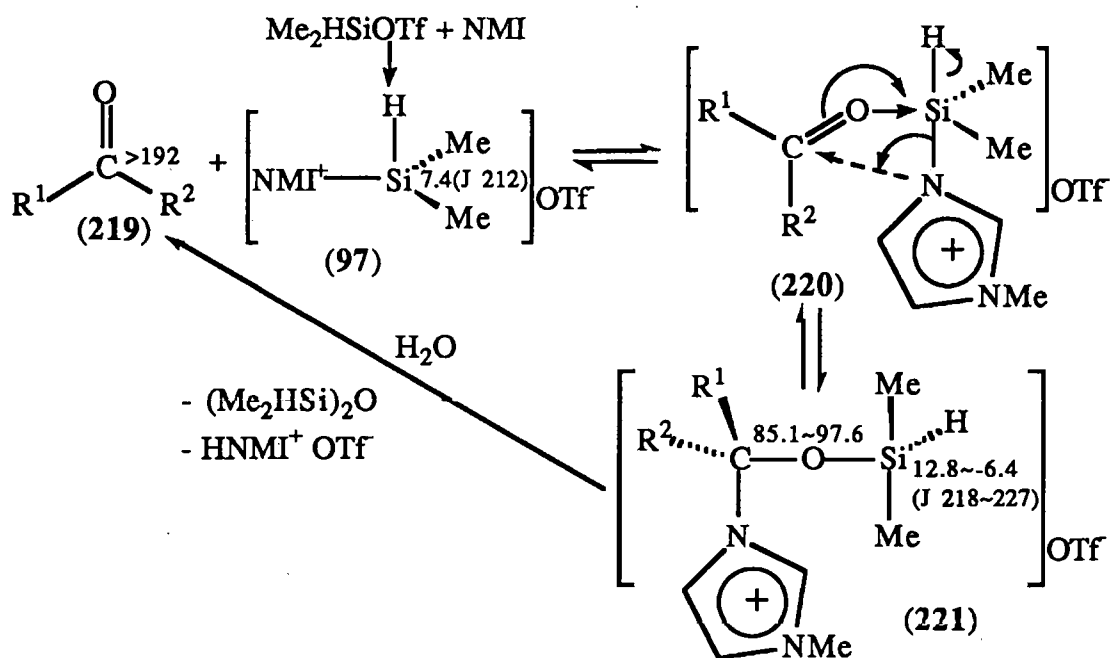
6.3 Reaction of $\text{R}^1\text{R}^2\text{C}=\text{O}$ with $\text{Me}_{3-n}\text{HSiOTf}_n$ -nucleophile species

There were at least two reasons to study the reaction of $\text{R}^1\text{R}^2\text{C}=\text{O}$ with $\text{Me}_{3-n}\text{HSiOTf}_n$ -nucleophile species. Firstly, tetra- and extracoordinated silane-

nucleophile species were suggested to be more reactive than the silane itself^{4, 5}, pentacoordinated complexes were especially speculated to have activated Si-H bonds^{128~132, 152}. In addition, the reduction of carbonyl groups by $\text{Me}_{3-n}\text{HSiOTf}_n$ needs modification to control the final products.



The mixture of equimolar Me_2HSiOTf and NMI in solution was proved to be a tetracoordinated salt $[\text{Me}_2\text{HSiNMI}^+]\text{OTf}^-$ ⁵¹. Solution NMR studies of the ^{13}C , ^1H and ^{29}Si nuclei indicated that the addition of aldehydes or ketones into such a solution established an equilibrium, in which a new complex was found with the oxygen of the carbonyl groups bonded to silicon while the imidazole group immigrated from Si to the carbonyl carbon, as illustrated in Scheme 6.6 and Table 6.1. In the ^{13}C NMR spectra, there were new signals in the range of 85.1~97.6 ppm replacing those of the carbonyl groups at the low field, together with a slight change of the values of other ^{13}C signals. The ^{29}Si and ^1H resonances also showed changes but the Si-H bond remained unbroken. The new signals were nearly natural width and were almost the only ones



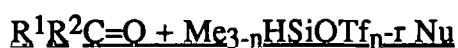
Scheme 6.6 Summary of the reaction of $\text{R}^1\text{R}^2\text{CO}$ with $[\text{Me}_2\text{HSi(NMI)}]^+\text{OTf}^-$ in CDCl_3 .

Table 6.1 NMR data of the mixtures of R¹R²CO with [Me₂HSiNMI⁺]OTf⁻ in CDCl₃.

R ¹	R ²	I** (%)	Chemical shifts (ppm)		
			²⁹ Si / (J, Hz)	¹³ C	¹ H
Me	Me	70	1.2/ (J 219) *-4.5/ (J 219)	137.4, 124.2, 123.8 36.4(NMI); 90.6, 30.1; -0.52 *137.8, 129.1, 120.2, 33.3(NMI); 206.9, 30.8; 0.57	9.08, 7.57, 4.02(NMI); 1.90; 4.76(q), 0.33(d) *7.43, 7.00, 6.87, 3.67; 2.14; 4.70(q), 0.20(d)
<i>t</i> Bu	Me	70	-6.3/ (J 218) *-4.6/ (J 204)	138.7, 124.3, 123.6, 35.7(NMI); 97.6, 40.6, 26.3, 24.8; -2.2 *213.9, 44.3, 26.4, 24.6; 0.52	8.77, 7.53, 7.42, 3.99(NMI); 2.14, 1.44; 5.05(q), 0.70(d) *2.13, 1.14; 4.70(q), 0.20(d)
Ph	H	85	11.9/ (J 227) *-4.6/ (J 226)	137.0, 124.3, 119.5, 36.4(NMI); 134.8, 130.4, 129.3, 126.1, 85.1; -2.0 *192.2, 136.6, 134.4, 129.7, 129.0; 0.52	9.24; 7.53~7.00(mt), 3.97; 4.72(q), 0.27(d) *9.98, 7.80(mt), 7.54(mt); 4.71, 0.20(d)
<i>t</i> Bu	H	95	12.8/ (J 227) *-4.6/ (J 205)	135.2, 123.6, 120.8, 36.5(NMI); 91.9, 37.2, 24.2; -2.2 *205.7, 42.5, 23.4; 0.52	7.63, 7.55, 4.05(NMI); 9.15, 0.96; 4.62(mt), 0.23(d) *9.47, 1.07; 4.7(q), 0.20(d)

* NMR data of the organic phase after hydrolysis of the mixture. ** I, approximate intensities of the new signals relative to those signals of unreacted species, which is not quoted in the table. For example, the chemical shifts (ppm) of [Me₂HSiNMI⁺]OTf⁻ were 7.4 (J 212Hz) for ²⁹Si; 139.5, 124.9, 123.9, 35.9 for ¹³C and 8.90, 7.57, 7.46, 4.02, 5.06(qu), 0.73(d) for ¹H NMR.

visible at normal intensity. These observations suggest that both **219** and **97** were involved in formation of a new complex which was in very slow exchange with the starting material and did not result in reduction. Indeed, the carbonyl groups, together with $\text{NMIH}^+\text{OTf}^-$ and $(\text{Me}_2\text{HSi})_2\text{O}$, were totally recovered after the addition of water into the mixtures. Therefore the most reasonable explanation of the reaction is the formation of complex **221** in the equilibrium, probably by way of **220**. The tetracoordinated salt of NMI (**97**) does not activate the Si-H bond but induces migration of NMI. There was no reaction at all if aldehydes or ketones were put together with NMI in CDCl_3 solution even in the presence of HOTf.



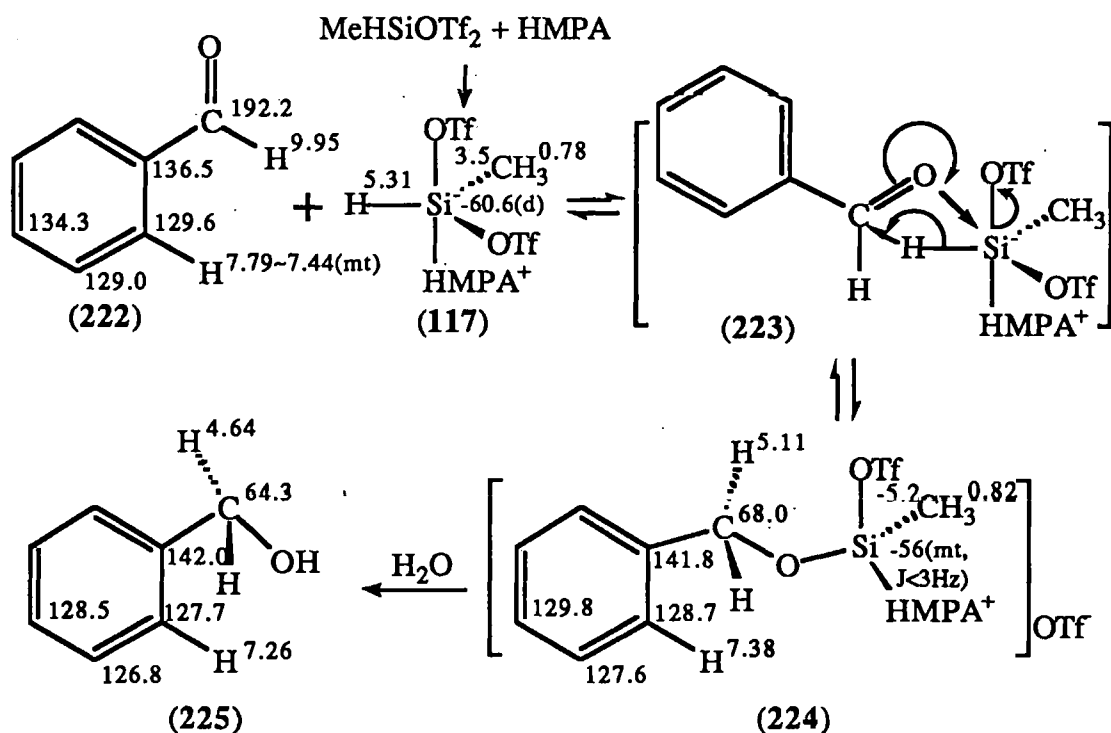
(i) Tetracoordinated silicon species.

The transfer of the coordinated nucleophile, Nu, from a tetracoordinated silicon to a carbonyl carbon was affected by both the steric hindrance of the species involved, and the electronic properties of the nucleophiles. Take the steric effect for example. NMR studies showed that benzophenone Ph_2CO did not react with $[\text{Me}_2\text{HSi}(\text{NMI})^+]\text{OTf}^-$ at all and neither did the mixture of benzaldehyde and the tetracoordinated adducts $[\text{Me}_2\text{HSi}(\text{HMPA})^+]\text{OTf}^-$. The most likely reason is that the large size of the R groups (Ph) or the nucleophile (HMPA) would make the intermediate equivalent to **220** so crowded that there would be no such intermediate formed.

Electronically, it is found with weak nucleophiles, such as DMF, that it was the reactivity of the Si-H bond that had been modified. The mixture of benzaldehyde PhCOH and $[\text{Me}_2\text{HSi}(\text{DMF})^+]\text{OTf}^-$ in CDCl_3 resulted in a smooth reduction of the aldehyde into alkoxyl species. As DMF has a low donicity, it was not capable of continuing to attack the carbonyl carbon. Instead it decelerated the violent reaction caused by the triflate group just like chloride did. Benkeser¹²¹ showed that Me_2HSiCl alone was inert to aldehydes.

(ii) Pentacoordinated silicon species.

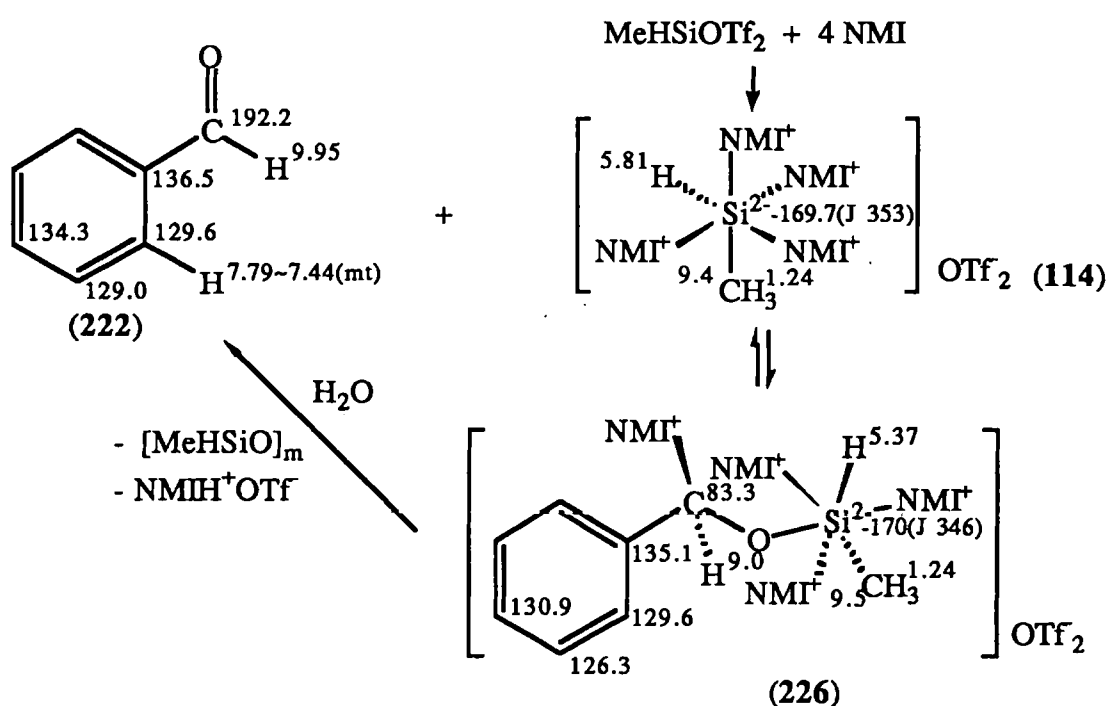
The extracoordinated Si-H containing species had similar reaction properties towards aldehydes and ketones. NMR studies showed that the mixing of the pentacoordinated dimethyl species $[\text{Me}_2\text{HSi}^-(\text{NMI})_2]\text{OTf}^-$ with benzaldehyde PhCOH resulted in a complex exactly the same as in the case of PhCOH with the tetracoordinated adduct $[\text{Me}_2\text{HSi}(\text{NMI})^+]\text{OTf}^-$, eg. complex **221**, only with a much larger equilibrium constant as the resonance signals of the carbonyl group could hardly be observed for the former. However, the pentacoordinated methylditriplate adduct $[\text{MeHSi}^-\text{OTf}_2(\text{HMPA})^+]$ reduced PhCOH into alkoxyl species smoothly and benzyl alcohol was obtained after hydrolysis of the mixture as shown in Scheme 6.7. A loose hexacoordinated silicon intermediate **223** was possibly involved. Nonetheless, the pentacoordinated complex **117** decreased the reactivity of the Si-H bond as the violent reaction of the silane itself was prevented.



Scheme 6.7 Reduction of PhCOH by $[\text{MeHSi}^-\text{OTf}_2(\text{HMPA})^+]$ in CD_3CN .

(iii) Hexacoordinated silicon species.

The reaction of hexacoordinated Si-H containing species $[\text{MeHSi}(\text{NMI})_4]^{2+} \text{OTf}^-_2$ (114) with benzaldehyde PhCOH was found by NMR studies to behave analogously to the pentacoordinated species $[\text{Me}_2\text{HSi}(\text{NMI})_2]^+ \text{OTf}^-$ and to the tetracoordinated adduct $[\text{Me}_2\text{HSi}(\text{NMI})]^+ \text{OTf}^-$. No reduction reaction was observed after hydrolysis of the mixture. Nevertheless the hexacoordinate nature of the silicon remained unchanged with a Si-O bond replacing a Si-N bond as shown in Scheme 6.8.



Scheme 6.8 Interaction of $[\text{MeHSi}(\text{NMI})_4]^{2+} \text{OTf}^-_2$ with PhCOH in CD_3CN .

Summary

The formation of Si-H containing silane-nucleophile adduct, either tetra- or penta- or hexa-coordinated, deterred the violent reaction of the silane with aldehydes or ketones, possibly because the substitutions of the triflate groups prevented the production of the most reactive cation $\text{R}^1\text{R}^2\text{HC}^+$ (218) and led to a smooth reduction of the carbonyl groups. However the adducts formed by NMI caused a different reaction

of the complexes with aldehydes and ketones, in which a Si-N bond was broken and an NMI molecule was transferred to the carbonyl carbon. No reduction reaction took place in this case and hydrolysis reformed the original carbonyl compound.

6.4 Reduction of $R^1R^2C=O$ with $Me_2HSiOTf$ in the presence of salts

It was found by chance that the reduction of aldehydes and ketones by $Me_2HSiOTf$ in the presence of triflate salts, such as $Bu_4N^+OTf^-$ and $DBPyH^+OTf^-$, was much less violent and the reaction was able to be brought under control. Some of the reactions were examined by NMR as shown in Table 6.2.

The results of the reduction of $R^1R^2C=O$ with $Me_2HSiOTf$ in the presence of tetrabutylammonium triflate Bu_4NOTf are comparable with those without such triflate salt. In both cases, Me_3CCOH and Me_2CO resulted in ether, Me_3CCOMe produced alcohol and Ph_2CO produced Ph_2CH_2 (see Entry 1, 7, 6 and 4 of Table 6.2). The advantage of the presence of triflate salt was reflected by the reduction of benzaldehyde or acetophenone by $Me_2HSiOTf$, which had been too violent to obtain selected reduction products. The reduction of $PhCOH$ and $PhCOMe$ with $Me_2HSiOTf$ into ether or alcohol was observed by ^{13}C and 1H NMR by use of triflate salts (see Entry 2, 3 and 5). It is likely that these ether and alcohol were formed before hydrolysis in some cases.

The presence of triflate salts was perhaps to stabilize the ions (such as **218**) produced in the reduction, rather than to alter the reaction pathway. The same complicated products were produced after days even in the presence of the salts for $PhCHO$ and $PhCOMe$. Alcohols or ethers could be changed into complicated species in such reacting system as it is found that either $PhCH_2OH$ or $(PhCH_2)_2O$ reacted to give complex mixtures, which had the same ^{13}C and 1H NMR signals as those from $PhCOH$, when it was added into the reacting system of Me_3CCOH with $Me_2HSiOTf$ in the presence of Bu_4NOTf and kept at room temperature for a couple of

Table 6.2 NMR data of the reaction of R^1R^2CO with $Me_2HSiOTf$ in the presence of $t\text{-Bu}_4\text{NOTf}$ in $CDCl_3$

No	R^1/R^2	r'	time (hr)	Chemical shifts (ppm)			Note
				$^{29}\text{Si}/$ (J Hz)	^{13}C	^1H	
1	$t\text{Bu}/\text{H}$	0.2	2	1.1/ (J<7)	58.8, 23.9, 19.7, 13.4(BuN); 82.5(CH_2), 32.5, 26.8; -0.5	3.00, 1.50, 0.99(sbr, BuN); 3.10, 0.95; 0.24	hydrolysis
				-19.1~ -21.9 (J<8)	58.5, 23.8, 19.6, 13.6(BuN); 81.9, 32.3, 26.8(ether); 0.8(mt)	3.00, 1.50, 1.00(sbr, BuN); 3.02, 0.90; 0.08	
2	Ph/H	1.0	3	1.6/ (J<7)	138.4, 128.4, 127.8, 127.6, 72.3; -0.7**	7.31, 4.52; 0.49**	mixtures in four days. Hydrolysis
				**	138.3, 128.5, 127.8, 126.9; 72.3(CH_2 , ether)	7.25, 4.47	
3	Ph/H	0.12 + 0.2*	2	8.1/ (J<4)	164.8, 148.0, 126.2, 37.2, 29.0(DBPyH ⁺); 138.6, 128.7, 128.5, 127.0, 66.3 (75%, alcohol); 138.5, 129.1, 128.0, 127.9, 72.3 (25%, siloxyl); -2.1	7.30, 4.88 (75%, alcohol), 4.52(25%, siloxyl); 8.4~7.8(mt), 1.34(DBPyH ⁺); 0.46	mixtures in two days
4	Ph/Ph	0.34	480	2.4/ (J<8)	142.1, 129.3, 129.1, 126.6; 42.7(CH_2), -0.1	7.19, 3.90; 0.59	in $CD_3\text{CN}$ hydrolysis
					141.9, 129.3, 129.0, 126.6, 42.2(Ph_2CH_2)	7.16, 3.86	
5	Ph/Me	1.0	18	-19.1~ -21.4 (J<7)	137.8, 128.7, 128.5, 126.3, 78.9; 0.8	7.26, 4.6(s), 2.67(s); 0.10	mixtures in three days hydrolysis
					137.8, 128.4, 127.3, 126.2, 77.8(CH , ether)	7.25, 4.65(q), 2.52(d)	
6	$t\text{Bu}/\text{Me}$	0.21	2	4.4/ (J<6)	79.0(CH), 35.3, 25.6 18.1; -1.5	3.76(q), 1.16(d), 0.88; 0.48	alcohol after hydrolysis
					75.5, 34.9, 25.5, 17.9	3.46(q), 1.12(d), 0.89	
7	Me/Me	0.19	120	-1.5/ (J<8)	74.68(CH), 22.0; -0.3	4.13(qu), 1.35(d); 0.48	ether after hydrolysis
					68.5, 22.9(ether)	3.64(qu), 1.16(d)	

*0.2 equivalent of 2,6-di-*tert*-butylpyridine triflate (DBPyH⁺OTf⁻) was present. **The NMR data of ^{29}Si , ^{13}C and ^1H of DBPy and the siloxane are not quoted again as they were nearly constant.

days. Therefore the medium was of considerable importance in the reduction of aldehydes and ketones by H-Si containing silane.

6.5 Miscellaneous reactions

Although H-Si containing silyl triflate species were capable of reducing aldehydes and ketones, they were not able to reduce acids, esters, amides and alkynes without catalyst (see Table 7.5).

PhCOOH + Me₂HSiOTf

The reaction of benzoic acid PhCOOH with Me₂HSiOTf in a mixture solvent of CD₃CN and CDCl₃ was not of reduction but silylation followed by disproportionation. NMR study of the mixture showed that the ²⁹Si resonance shifted from 23.2 ppm to 13.8 ppm together with the Si-H coupling decreasing from 239 Hz to less than 7 Hz after the sample had been kept for twenty days. In the proton spectra, the signals of the acid proton (13.3 ppm) and the Si-H proton of the silane (4.96 ppm, mt) also disappeared. Meanwhile the ¹³C resonance of the benzoic acid remained unchanged. A pressure increase in the sample tube was also observed. Therefore there was no reduction as shown in Equation 6.3.



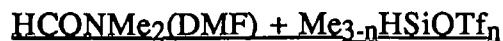
Equation 6.3

MeCOOEt + Me₂HSiOTf

There was no reaction found by NMR study of the mixture of MeCOOEt and Me₂HSiOTf in CDCl₃ as shown in Equation 6.4. The NMR properties of ²⁹Si, ¹³C and ¹H of the mixture remained unchanged even after fifteen days.



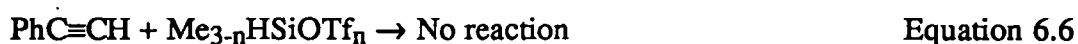
Equation 6.4



The interaction of DMF with MeHSiOTf₂ has been proved to be a decomposition process of the Si-H bond without reduction (see Table 2.22). The mixture of DMF and Me₂HSiOTf in CDCl₃ examined by NMR was found to be only a substitution reaction. The NMR spectra showed the Si-H bond remained and DMF coordinated as illustrated in Equation 6.5. The adduct was stable as no change of its NMR properties was observed after five days.



Phenylacetylene was found to be inert to Me_{3-n}HSiOTf_n by NMR study as shown in Equation 6.6. The ¹³C and ¹H NMR signals of phenylacetylene of the mixtures of PhC≡CH with Me₂HSiOTf or MeHSiOTf₂ stayed constant. The addition of triflate salts, such as Bu₄NOTf, or nucleophiles, such as three molar equivalents of NMI, made no difference.



Summary

The fact that there was no reduction reaction in the mixtures of Me_{3-n}HSiOTf_n and PhCOOH or MeCOOEt or HCONMe₂ or PhC≡CH perhaps suggests that it is very important for the oxidizer to be able to attack the silicon initially and to form an extracoordinate intermediate. The non-reaction of MeCOOEt or PhC≡CH with Me_{3-n}HSiOTf_n may be because of lack of nucleophilic reaction in the first place while the non-reduction of PhCOOH or HCONMe₂ by Me_{3-n}HSiOTf_n was possibly caused by the delocalized positive charge at the carbonyl carbon.

6.6 Summary — the reduction of aldehydes and ketones by Si-H bonds

Solution NMR study has shown that Si-H containing methylsilyl triflates $\text{Me}_{3-n}\text{HSiOTf}_n$ ($n = 1, 2$) are good reducing agents for, and only for, aldehydes and ketones R^1COR^2 ($\text{R}^1 = \text{Ph, Me, } i\text{Bu}$; $\text{R}^2 = \text{Ph, Me, H}$). The reduction of the carbonyl groups was affected by the silanes, R^1 , R^2 groups of the carbonyl group bonded, the reaction media and the conditions.

The mechanisms

The readiness of the reduction of aldehydes and ketones by Si-H containing methylsilyl triflates supports the suggestion that electronegative groups on silicon increase the reducing reactivity of the silane²⁴. For example, the less electronegative chlorine led Me_2HSiCl to be inert to carbonyl groups¹²¹. However, the reaction mechanisms may be different with different silanes under different reaction conditions. The formation of hypercoordinate intermediates was generally most convincing while other ionic species were only suggested in special cases, such as Et_3SiH as a H^- supplier in acidic solution^{117~120} and $(\text{R}_3\text{N}^+\text{H} + ^-\text{SiCl}_3)$ with HSiCl_3 in bases^{121, 125}. For $\text{Me}_{3-n}\text{HSiOTf}_n$, it is more likely that penta- and hexa-coordinated species, such as complexes **215**, **217** and **223**, played a crucial part in the reductions of aldehydes and ketones. Therefore, the easiness of a Si-H containing silane to form hypercoordinated bonds with the oxidizer at silicon could be applied to estimate the readiness of the silane to initiate a reduction reaction. What is more, the simultaneous formation of a loose four-membered ring involving the Si-H bond, the donor oxygen atom and the carbonyl carbon was also important to help the Si-H bond to break and the C-H bond to develop. In addition, a cation $[\text{R}^1\text{R}^2\text{HC}^+]$ (**218**), which was extremely reactive and caused the reaction to be complicated, could be produced following an initial reduction. Factors affecting the formation of such hypercoordinated intermediates and their four-membered ring and the production and stabilization of the possible consequential cations may, therefore, determine the outcome of the reduction reactions.

The silanes

The readiness of the formation of hypercoordination at silicon is firstly controlled by the silane itself. The methylsilyl triflates $\text{Me}_2\text{HSiOTf}^{51}$ and MeHSiOTf_2 are known to be very reactive to nucleophiles and ready to expand the coordination at silicon while dimethylchlorosilane $\text{Me}_2\text{HSiCl}^{53}$ and trialkoxysilanes $(\text{RO})_3\text{SiH}$ were found inert to weak nucleophiles and even trichlorosilane HSiCl_3 had no significant reaction towards equimolar quantities of nucleophiles such as DMPU and DMF at room temperature. Therefore the former could act as reducing agents and the latter had no reaction with very weak nucleophiles, such as aldehydes and ketones, under normal conditions^{121, 152}.

The silane-nucleophile adducts

Pentacoordinated HMPA and tetracoordinated DMF complexes of H-Si containing species were effective reducing agents, presumably by the same mechanism as the silanes themselves. NMI-silane complexes, including tetra-, penta- and hexacoordinated ones, reacted with aldehydes and ketones but did not give reduction products. The products resulted from migration of NMI from Si to C, most likely by the same mechanism of H migration from Si to C. Therefore the readiness of transfer a group bonded to silicon to the carbonyl carbon is in the order of $\text{NMI} > \text{H} \gg \text{DMF}$, HMPA. No C-DMF nor C-HMPA bonds were observed in the mixtures of aldehydes or ketones with silane-DMF or silane-HMPA complexes, probably because of the low nucleophilicity in the case of DMF and the steric hindrance from the large size of the nucleophile in the case of HMPA.

However, there was an advantage in using HMPA and DMF complexes of $\text{Me}_{3-n}\text{HSiOTf}_n$ as reducing agents if the nucleophilic attack at the silicon by the carbonyl group was still sterically favoured. The Si-Nu bonds were able to offset the strong electron withdrawing effect from the Si-OTf bonds and thus prevented the formation of any cation (218). In this way, violent reaction could be avoided.

PhR²C=O (R² = H, Me)

The conjugation of the phenyl ring and the carbonyl group often led to a easy formation of the cation [PhR²HC⁺] in the reduction of PhCOR² by Me_{3-n}HSiOTf_n and complicated the outcome. Alcohols or ethers could only be selectively obtained by either offsetting the electron withdrawing power of the silane moiety using silane-nucleophile complexes, such as [Me₂HSi(DMF)⁺]OTf⁻ and [MeHSi⁻OTf₂(HMPA⁺)], or stabilizing the cation by adding triflate salts.

Ph₂C=O

The reduction of aldehydes and ketones by Me_{3-n}HSiOTf_n normally produced alkoxyl compounds even with excess silane or externally addition of Et₃SiH and only Ph₂CO was an exception as it was completely reduced to Ph₂CH₂, although the reduction process was very slow. This is probably because of the steric hindrance of the two phenyl groups, which contributed to the slowness of the reaction and helped to stabilize the cation and protected it from any other attack except H⁻.

R¹R²C=O (R¹ = *t*Bu, Me; R² = Me, H)

Alkyl aldehydes and ketones were selectively reduced to alkoxyl species by Me_{3-n}HSiOTf_n without complex by-products. The reactions were rapid, though the reduction of the ketones was a little slower than that of the aldehydes. An alcohol was always obtained from *t*BuCOMe after hydrolysis, probably because of the steric hindrance. However, a small amount of ether was produced in the reduction of acetone before hydrolysis, though the outcome of the reduction, either alcohol or ether, was largely affected by the homogeneity of the hydrolizing systems.

The media — the presence of salts

The existence of triflate salts, such as Bu₄N⁺OTf⁻ and DBPyH⁺OTf⁻, could lead the reduction of aldehydes or ketones by Me_{3-n}HSiOTf_n to be more smooth than without such salts, and delay the formation of unwanted products in case the of PhR²CO

($R^2 = \text{Me, H}$). Presumably the salts helped to stabilize any ionic species and to disperse the localized charges in the reaction system.

$R^1\text{COR}'$ ($R^1 = \text{Ph, Me, H}$; $R' = \text{OH, OEt, NMe}_2$); $\text{PhC}\equiv\text{CH}$

No reduction reaction was found between acids, esters, amines, alkynes with Si-H containing methylsilyl triflates. For MeCOOEt and $\text{PhC}\equiv\text{CH}$, it is probably because they lacked of the nucleophilicity required to attack the silane. For PhCOOH and HCONMe_2 , though the carbonyl oxygen was bonded to silicon, the positive charge was so widely delocalized that the carbonyl carbon was not further attacked by H^- .

In conclusion, the Si-H containing methylsilyl triflates $\text{Me}_{3-n}\text{HSiOTfn}$ are very promising and effective reducing agents for aldehydes and ketones. They are the first acyclic, simple silanes found to be useful in the reduction of carbonyl carbons without catalyst. Applications of these reducing agents in synthesis and even industry are expected.

Chapter 7 Experimental

7.1 Introduction

This work contains an intensive study of the interactions of multifunctional silanes with nucleophiles in solution by NMR spectroscopy and conductivity measurements. Syntheses of some of the silanes and analyses of the solid adducts are also involved. NMR studies of the reaction using Si-H bonds as reducing agents are performed in solution as well. All these experiments are described in the following sections by instrumentation, purification of chemicals, syntheses, NMR and conductivity studies of the interactions of silanes with nucleophiles and reactions of Si-H containing compounds.

7.2 Instrumentation and equipment

The silanes used, especially those of increased numbers of functional groups with good leaving ability, are extremely moisture sensitive. In order to eliminate contamination by moisture, all chemicals were treated as moisture sensitive compounds and handled under dry nitrogen (purchased from Air Products, high purity grade). Quantities of liquid compounds were measured and transferred via stainless steel needles and

Hamilton all glass-teflon, gas tight syringes. Solid compounds were handled in a Faircrest dry nitrogen glove box. A Sartorius 2000 MP digital balance was used to provide accurate weighings of up to ± 0.5 mg.

NMR parameters

All the NMR spectral measurements were made on a Jeol FX90Q NMR spectrometer with a tunable, multinuclear probe. Tetramethylsilane (TMS) was normally taken as the reference for the ^{29}Si , ^{13}C and ^1H NMR. ^{31}P and ^{19}F NMR were respectively related to H_3PO_4 and CCl_3F externally. The usual spectral parameters were shown in Table 7.1.

Table 7.1 NMR parameters for ^1H , ^{13}C , ^{29}Si , ^{19}F and ^{31}P .

	^1H	^{13}C	^{29}Si	^{19}F	^{31}P
Spectral width (Hz)	1000 or 2000	5302	4000 or 6000 or 8000	20000	5000
Frequency (MHz)	89.56	22.50	17.76	84.26	36.26
Pulse width (μs)	24	22	22	24	24
Pulse delay (s)	0.1	1.0	10 to 30	1.0	1.0
Irradiation mode	non-decoupling	complete decoupling	decoupling without nuclear Overhauser enhancement	complete decoupling	complete decoupling
Exponential window (Hz)	0.0	1.24	3.09	0.0	0.0

The ^{29}Si INEPT technique was used mainly for Si-H containing species and for the measurements of the ^{29}Si - ^1H coupling. Pulse width, pulse interval and pre-delay

settings were dependent on the magnitude of $J_{\text{Si-H}}^{137}$, values of 13 ms 13 μs and 13 ms respectively were found to be suitable in most cases.

^{13}C INEPT technique was employed to distinguish the kind of carbons (either CH_3 , or CH_2 , or CH , or C) in the study of reduction reactions of unsaturated organic compounds by Si-H containing species. Values of 2.5 seconds for pulse delay, 1.7 ms for pulse interval and 1.7, 3.4, 5.1 ms for pre-delay were satisfactory.

The temperature was set using a Jeol temperature controller (quoted temperature accuracy $\pm 2^\circ\text{C}$) in variable temperature studies.

Boiling temperatures

Boiling temperatures were read directly from the exit thermometer during distillations, the corresponding pressures were read directly from a vacuum gauge if reduced pressure was applied.

Melting temperatures

Melting temperatures were determined on a Buchi 510 melting point apparatus.

Microanalysis

Elemental analyses were carried out by MEDAC Ltd.

Conductivity

Conductivity measurements were carried out using a PTI-10 digital conductivity meter (quoted accuracy $\pm 0.5\%$, repeatability ± 1 digit) under nitrogen. Calibration of the meter was checked frequently with standard KCl solution.

7.3 Purification of chemicals

Purification of chemicals was mainly done by distillation. The pressure was adjusted to achieve a distillation temperature between 50-100°C if possible. In some cases, the

chemicals were simply stored over molecular sieves under nitrogen prior to use. The choice of drying agents and the purification procedure are summarized as follows:

(I) Chemicals stored over activated 4A molecular sieves under nitrogen at least two days prior to use without further purification:

tetramethylsilane (Aldrich Chemical Co. Ltd., 99.9%, NMR grade)
chloroform-d₁ (Aldrich Chemical Co. Ltd., 99.8 atom % D, GOLD LABEL)
dichloromethane-d₂ (Aldrich Chemical Co. Ltd., 99 atom % D, GOLD LABEL)
acetonitrile-d₃ (Aldrich Chemical Co. Ltd., 99 atom % D, GOLD LABEL)
nitromethane-d₃ (Aldrich Chemical Co. Ltd., 99 atom % D, GOLD LABEL)
benzene-d₆ (Aldrich Chemical Co. Ltd., 99.5 atom % D, GOLD LABEL)
benzoic acid (Aldrich Chemical Co. Ltd., 99%)
2,6-di-*tert*-butylpyridine (Aldrich Chemical Co. Ltd., 97%)
diethyl ether (BDH Chemical Ltd., 99%)
acetophenone (BDH Chemical Ltd. 99%)
pinacolone (Aldrich Chemical Co. Ltd., 98%)
trimethylacetaldehyde (Aldrich Chemical Co. Ltd., 97%)
benzaldehyde (Aldrich Chemical Co. Ltd., 98%)
phenylacetaldehyde (Aldrich Chemical Co. Ltd., 99%)
phenylacetylene (Aldrich Chemical Co. Ltd., 98%)
benzophenone (Aldrich Chemical Co. Ltd., 99%)
acetic acid, glacial (FSA Laboratory Supplies, HPLC grade)

(II) Chemicals used as purchased:

triphenylsilane (Aldrich Chemical Co. Ltd., 97%)
dimethylphenylsilane (Aldrich Chemical Co. Ltd., 99%)
diphenylmethylsilane (Aldrich Chemical Co. Ltd., 98%)
4-dimethylaminopyridine (Aldrich Chemical Co. Ltd., 99%)
HBr (UCAR Union Carbide, High purity)
iodine (Aldrich Chemical Co. Ltd., resublimed, 99.8+%)
aluminum (Aldrich Chemical Co. Ltd., Foil, GOLD LABEL)

antimony trifluoride (Aldrich Chemical Co. Inc., 99%)
calcium carbonate (Hopkin & Williams Ltd.)
potassium hydride (Aldrich Chemical Co. Inc, 35 wt. %)
tetrabutylammonium trifluoromethanesulfonate (Aldrich Chemical Co. Inc.,
99%)
diallyldimethylsilane (Aldrich Chemical Co. Inc., 98%)
bis(dimethylamino)dimethylsilane (Aldrich Chemical Co. Ltd., 96%)

(III) Chemicals distilled before use:

methyldichlorosilane (Aldrich Chemical Co. Ltd., 97%)
dimethyldichlorosilane (Aldrich Chemical Co. Ltd., 99%)
methyltrichlorosilane (Aldrich Chemical Co. Ltd., 98%)
diphenyldichlorosilane (Aldrich Chemical Co. Ltd., 96%)
triethylsilane (Silar Laboratories Inc)
silicon chloride (SIGMA Chemical Ltd.)
trifluoromethanesulphonic acid (Aldrich Chemical Co. Ltd., 99%)
phenyldichlorosilane (PCR Incorporated)
trichlorosilane (Aldrich Chemical Co. Inc., 99%)
phenylmethyldichlorosilane (Aldrich Chemical Co. Inc., 96%)
tetraethoxysilane (Aldrich Chemical Co. Ltd., Foil, GOLD LABEL)

(VI) Chemicals stood for a few days, distilled and stored over 4A molecular sieves:

1-methylimidazole (Aldrich Chemical Co. Ltd., 99%)
N,N-dimethylformamide (Aldrich Chemical Co. Ltd., 99%)
1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (Fluka AG, purum)
2-propanol (Aldrich Chemical Co. Ltd., HPLC grade)
acetonitrile (Aldrich Chemical Co. Ltd., HPLC)
dichloromethane (Aldrich Chemical Co. Ltd., HPLC grade)
acetone (Aldrich Chemical Co. Ltd., HPLC grade)

(V) Chemicals purified by individual routes:

hexamethylphosphoramide:- Aldrich Chemical Co. Ltd., 99%; distilled from phosphorus pentoxide (P_2O_5) and stored over 4A molecular sieves.

chloroform:- BDH Chemicals Ltd., 'Analar'; dried with potassium carbonate and distilled in the dark from calcium chloride, and finally stored under nitrogen in a light proof container over 4A molecular sieves.

n-hexane:- Rathburn Chemicals Ltd., HPLC grade, distilled from sodium wire and stored over fresh sodium wire and 4A molecular sieves.

benzene:- BDH Chemicals Ltd., 'AnalaR'; dried with calcium chloride prior to distillation.

tetrahydrofuran:- Rathburn, Chemicals Ltd., HPLC grade; refluxed and distilled from calcium hydride under nitrogen.

7.4 Syntheses of silanes

Silanes are extremely moisture sensitive. Therefore all synthesis operations were carried out in sealed systems free of air, protected by nitrogen.

Syntheses of silyltriflates

Silyltriflates can be synthesized by reacting silanes with trifluoromethanesulphonic acid (triflic acid, HSO_3CF_3)^{153, 154}. Stoichiometric quantities of triflic acid were added dropwise to the respective silane solutions, with stirring, under an atmosphere of dry nitrogen and ice-bath. High temperature afterwards was necessary to make multi-triflate silanes in some cases. 1H NMR was used to follow the reaction and, prior to distillation, indicated essentially quantitative formation of the products. Distillation of the mixtures resulted in colourless liquids, which were identified by NMR spectroscopy in $CDCl_3$.

(I) Synthesis of Me₂HSiOTf

Phenyldimethylsilane 47.56 g (0.35 mol.); Triflic acid 52.58 g (0.35 mol.)

Yield, 59.2 g; 81%

b.p., 125±3°C / 760 mmHg (Lit.¹⁵³ 123°C / 760 mmHg)

NMR (δ , ppm),

²⁹Si: 24.52 (J 247 Hz)

¹³C: 139.76, 125.69, 111.62, 98.02 (q, CF₃); -1.55 (MeSi)

¹H: 5.00 (mt, J 2.9 Hz, 1H, SiH); 0.59 (d, J 2.9 Hz, 6H, MeSi)

NMR data identical to literature values¹⁵³.

(II) Synthesis of Me₂SiOTf₂

Dimethyldichlorosilane 12.7 ml (0.105 mol.); triflic acid 31.34 g (0.209 mol.);
110±10°C for 20 hours before distillation.

Yield, 33.5 g; 90%

b.p., 86±2°C / (10.2±0.3) mmHg

NMR (δ , ppm),

²⁹Si: 14.65

¹³C: 139.37, 125.23, 111.16, 97.03 (q, CF₃); -1.15 (MeSi)

¹H: 0.86 (MeSi)

(III) Synthesis of MeHSiOTf₂

Methyldiphenylsilane 12.0 g (0.059 mol.); triflic acid 10.5 ml (0.119 mol.);
80±5°C for 12 hours before distillation.

Yield, 13.1 g; 91% (purity > 95%)

b.p., 75±1°C / 5 mmHg

NMR (δ , ppm),

²⁹Si: -8.23 (J 296 Hz)

^{13}C : 141.43, 127.30, 113.23, 99.10 (q, CF_3); -1.90 (MeSi)

^1H : 5.32 (q, J 2.0 Hz, 1H, SiH); 0.96 (d, J 2.0 Hz, 3H, MeSi)

(IV) Synthesis of PhHSiOTf_2

triphenylsilane 25.5 g (0.098 mol. dissolved in 30 ml CHCl_3); triflic acid 30.37 g (0.202 mol.); the reaction completed at room temperature. The solvent and C_6H_6 were evaporated under reduced pressure.

Yield, 39.0 g; 98% (purity > 95%)

NMR (δ , ppm),

^{29}Si : -28.20 (J 323 Hz)

^{13}C : 139.53, 125.41, 111.27, 97.14 (q, CF_3); 135.00, 134.20, 129.43, 128.45 (PhSi)

^1H : 5.69(1H, SiH); 7.35, 7.64 (mt, 5H, PhSi)

NMR data matches the literature values¹⁵⁴.

(V) Synthesis of MeSiOTf_3

Methyltrichlorosilane 5.0 ml (0.043 mol.); triflic acid 21.6 g (0.144 mol.); Mixed at 0°C ; $65\pm 5^\circ\text{C}$ for 20 hours; $105\pm 5^\circ\text{C}$ for 24 hours and $160\pm 5^\circ\text{C}$ for 24 hours before distillation.

Yield, 7.2 g; 34%

b.p., $87\pm 1^\circ\text{C}$ / 3.8 ± 0.1 mmHg

NMR (δ , ppm),

^{29}Si : -51.73

^{13}C : 139.65, 125.46, 111.34, 97.23 (q, CF_3); -3.91 (MeSi)

^1H : 1.21 (MeSi)

(VI) Synthesis of HSiOTf_3

Triphenylsilane 25.71 g (0.099 mol. dissolved in 30 ml CHCl_3); triflic acid 44.7 g (0.298 mol.);

The reaction completed at room temperature; a extremely moisture sensitive liquid was collected as CHCl_3 and C_6H_6 were evaporated under reduced pressure and high temperature (oil-bath 150°C / 0.5 mmHg for 1.5 hours).

Yield, 43.5 g; 92% (purity > 90%)

NMR (δ , ppm),

^{29}Si : -76.04 (J 416.0 Hz)

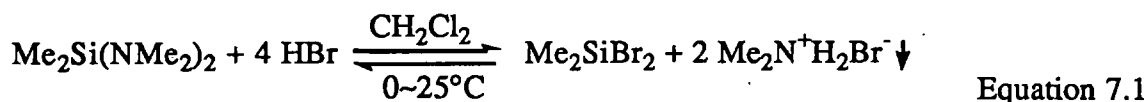
^{13}C : 139.48, 125.79, 111.33, 96.97 (q, CF_3)

^1H : 5..47(HSi)

Syntheses of other multifunctional silanes

(VII) Synthesis of Me_2SiBr_2

Me_2SiBr_2 was made as illustrated by equation 7.1:



Bis-(dimethylamino)dimethylsilane 52.25 g (0.357 mol.) added to 100 ml CH_2Cl_2 . HBr gas was bubbled in with stirring at 0°C and switched to room temperature (when white fume formed at the exit of the system) until no $\text{Me}_2\text{Si}(\text{NMe}_2)_2$ left . The solution was distilled after filtration.

Yield, 39.60 g; 39.6%

b.p., $112\pm 1^\circ\text{C}$ / 760 mmHg

NMR (δ , ppm),

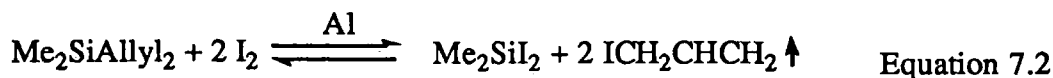
^{29}Si : 19.86

^{13}C : 9.59

^1H : 1.10 (MeSi)

(VIII) Syntheses of Me_2SiI_2

Me_2SiI_2 was made as shown by the following equation (Equation 7.2):



Diallyldimethylsilane 23.2 ml (0.127 mol.) was mixed with iodine 53.47 g (0.250 mol.); 0.2 g aluminum was added at 0°C with stirring. 0°C for two hours and 100±10°C for two hours.

Yield, 20.5 g; 51%

b.p., 162±1°C / 760 mmHg

NMR (δ , ppm; in mixture solvent of CD₃CN and CDCl₃),

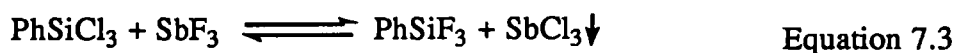
²⁹Si: -31.27

¹³C: 13.27

¹H: 1.59 (MeSi)

(IX) Synthesis of PhSiF₃

PhSiF₃ was prepared by exchange reaction as shown in Equation 7.3 :



Antimony trifluoride 11.11 g (0.062 mol.) was added to 20 ml CHCl₃; PhSiCl₃ 9.76 ml (0.061 mol.) was injected dropwise with stirring at 0°C; 72±2°C for two and half hours.

Yield, 4.3 g; 43%

b.p., 100±1°C / 760 mmHg

NMR (δ , ppm),

²⁹Si: -50.31, -65.34, -80.31, -95.35 (q, J_{Si-F} 267.6)

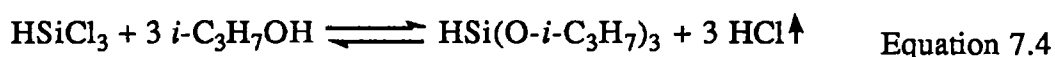
¹³C: 134.77, 133.56, 128.85, 128.57

¹⁹F: -141.55

¹H: 7.69~7.47 (mt, PhSi)

(X) Synthesis of HSi(O-*i*-Pr)₃

HSi(O-*i*-Pr) was made by alcoholysis as illustrated in Equation 7.4:



Trichlorosilane 5 ml (0.15 mol.) was mixed with 10 ml benzene; 2-propanol 11.1 ml (0.15 mol.) was injected dropwise with stirring at 0°C; Stayed overnight at room temperature.

Yield, 5.2 g; 51%

b.p., 72±1°C / 760 mmHg

NMR (δ , ppm),

^{29}Si : -62.43 ($J_{\text{Si-H}}$ 282.2)

^{13}C : 65.37, 25.51

^1H : 4.32 (q, J 6.1 Hz, 1H, HSi), 1.25 (3H), 1.18 (18H)

7.5 Interactions and coordination chemistry of silanes with nucleophiles

The nucleophilic reaction mechanisms and coordination chemistry of silanes with nucleophiles were based on the solution NMR studies of a series silane-nucleophile mixtures, some of the solid adducts analyses and solution conductivity titrations.

7.5.1 Solution NMR studies of the interactions of silanes with nucleophiles

General procedure

All compounds including the silanes, the nucleophiles and the solvents were handled under nitrogen. Normal techniques used for handling moisture sensitive compounds were employed. In the titration studies, each silane was first measured and transferred with a syringe, additionally weighed if the specific gravity of the silane was not accurate, into two millilitres of solvent or solvents in a 10 mm NMR tube. Successive aliquots of nucleophiles were then injected. NMR data of the mixtures were collected for each stoichiometry. The interactions of DMAP were mostly done by titrating DMAP (weighed and dissolved in two millilitre solvents) with silane as it is more convenient.

Cooperative and competitive reactions were carried out in a similar way. With cooperative reactions (one silane with two nucleophiles), the sequence of the additions of nucleophiles was random. The two silanes were firstly mixed in a solvent with the competitive reactions (two silanes with one nucleophile). NMR spectra were run after every addition.

Low temperature studies were monitored by a Jeol temperature controller. Solubility of the components under study was investigated, prior to the experiment, by cooling the sample in a carbon dioxide/acetone bath (-78°C). NMR spectra were recorded at various temperatures. More than five minutes were allowed after each readjustment of temperature for the solution to reach thermal equilibrium.

Selection of the solvents

Chloroform-d₁ was always the first choice of the interactions for economic reasons. If the silane-nucleophile adducts were insoluble in CDCl₃, other solvents such as CD₃CN, CD₂Cl₂ or even a mixture solvent were employed. In these case, the selection of solvents was done prior to NMR studies.

NMR study of individual interactions

The valuable NMR data of the mixtures of each silane with nucleophiles are either listed in tables or illustrated in figures or schemes as summarised below:

<u>Me₂SiCl₂</u>	+ r NMI:	Figure 2.1 & 2.2; Table 2.1 & 2.10; Scheme 2.17 & 2.19 & 2.20 & 3.12;
	+ r DMAP:	Figure 2.1; Table 2.1;
	+ r DMF:	Figure 2.1; Table 2.1;
	+ r HMPA:	Figure 2.1; Table 2.1 & 2.10; Scheme 2.21 & 3.14;
	+ r DMPU:	Table 2.1.
<u>Me₂SiBr₂</u>	+ r NMI:	Figure 2.4; Table 2.2 & 2.10;
	+ r DMAP:	Table 2.2;

	+ r DMF:	Figure 2.6 & 2.6;
	+ r HMPA:	Table 2.3 & 2.10;
	+ r DMPU:	Figure 2.6 & 2.6.
<u>Me₂SiI₂</u>	+ NMI:	Figure 2.9 & 2.10; Table 2.10
	+ r DMF:	Table 2.5;
	+ r HMPA:	Table 2.4 & 2.10; Scheme 2.18;
	+ r DMPU:	Table 2.6.
<u>Me₂SiOTf₂</u>	+ NMI:	Figure 2.12 & 2.13 & 2.18; Table 2.8 & 2.9 & 2.10; Scheme 2.20;
	+ r DMAP:	Figure 2.18; Table 2.8 & 2.9;
	+ r DMF:	Figure 2.14 & 2.15 & 2.18; Table 2.8 & 2.9;
	+ r HMPA:	Figure 2.18; Table 2.7 & 2.8 & 2.9 & 2.10; Scheme 2.18 & 2.21 & 3.14;
	+ r DMPU:	Figure 2.14 & 2.18; Table 2.8 & 2.9.
<u>MePhSiCl₂</u>	+ r NMI:	Figure 2.19 & 2.20; Table 2.11;
	+ r DMAP:	Table 2.12;
	+ r DMF:	Table 2.12;
	+ r HMPA:	Figure 2.19; Table 2.12;
	+ r DMPU:	Table 2.12.
<u>Ph₂SiCl₂</u>	+ r NMI:	Figure 2.22 & 2.23; Table 2.13; Scheme 2.17 & 2.19;
	+ r DMAP:	Table 2.13;
	+ r DMF:	Table 2.13;
	+ r HMPA:	Table 2.13;
	+ r DMPU:	Table 2.13.
<u>MeHSiCl₂</u>	+ r NMI:	Table 2.14; Scheme 2.19 & 2.20 & 3.13;
	+ r DMAP:	Table 2.15 & 2.16; Scheme 2.9;
	+ r DMF:	Table 2.15 & 2.16;

	+ r HMPA:	Figure 2.26; Table 2.17; Scheme 2.21;
	+ r DMPU:	Figure 2.26; Table 2.17.
<u>PhHSiCl₂</u>	+ r DMAP:	Table 2.15 & 2.16;
	+ r DMF:	Table 2.15 & 2.16;
	+ r HMPA:	Figure 2.26; Table 2.17;
	+ r DMPU:	Figure 2.26; Table 2.17.
<u>MeHSiOTf₂</u>	+ r OTf:	Table 2.19;
	+ r NMI:	Table 2.20; Scheme 2.20;
	+ r DMAP:	Table 2.22;
	+ r DMF:	Table 2.22;
	+ r HMPA:	Table 2.23; Scheme 2.21;
	+ r DMPU:	Table 2.25.
<u>PhHSiOTf₂</u>	+ r NMI:	Table 2.21;
	+ r DMAP:	Table 2.22;
	+ r DMF:	Table 2.22;
	+ r HMPA:	Table 2.24;
	+ r DMPU:	Table 2.26.
<u>MeSiCl₃</u>	+ r NMI:	Table 3.1; Scheme 3.13;
	+ r DMAP:	Table 3.2;
	+ r DMF:	Table 3.2;
	+ r HMPA:	Figure 3.9; Table 3.3; Scheme 3.14;
	+ r DMPU:	Table 3.3.
<u>MeSiOTf₃</u>	+ r NMI:	Table 3.4;
	+ r DMF:	Table 3.5;
	+ r HMPA:	Table 3.6;
	+ r DMPU:	Table 3.7.

PhSiCl₃ + r NMI: Table 3.8; Scheme 3.12;
 + r DMAP: Table 3.9;
 + r DMF: Table 3.9;
 + r HMPA: Figure 3.9; Table 3.10.

PhSiF₃ + r NMI: Table 3.11;
 + r DMF: Table 3.12;
 + r HMPA: Table 3.13;
 + r DMPU: Table 3.14.

HSiCl₃ + r NMI: Table 3.15;
 + r DMF: Table 3.16;
 + r HMPA: Table 3.17;
 + r DMPU: Table 3.18.

HSiOTf₃ + r NMI: Table 3.19;
 + r DMAP: Table 3.20;
 + r DMF: Table 3.20;
 + r HMPA: Table 3.21;
 + r DMPU: Table 3.22.

HSi(O-*i*Pr)₃ + r NMI: Table 3.23.

SiCl₄ + r NMI: Table 4.1;
 + r DMF: Table 4.2;
 + r HMPA: Table 4.3;
 + r DMPU: Table 4.4.

Miscellany

(I) $\delta^{29}\text{Si}$ values (ppm) of silane complexes using NMI as solvent, externally locked:

Me₂SiCl₂ (0.2 ml), -68.0;

Me₂SiBr₂ (0.1 ml), -70.4;

Me₂SiI₂ (0.05 ml), -68.0;

Me₂SiOTf₂ (0.1 ml), -70.4.

(II) Some of the NMR data of r DMAP interacting with silanes:

Me₂SiI₂, r = 5.2, c = 0.1 in CD₃CN+CDCl₃, a lot of solid present in the solution:

δ²⁹Si, Null;

δ¹H(ppm), 8.95, 6.62(d), 3.02, 0.85(all were weak and broadened).

MeSiOTf₃, c = 0.07 in CD₃CN+CDCl₃:

	δ ²⁹ Si(ppm)	δ ¹ H(ppm)
r = 1,	-111.20	8.04(d), 6.88(d), 3.23, 1.07
r = 6,	Null	8.08(d), 6.71(d), 3.15, 0.8(vbr)

PhSiF₃, r = 6.6, c = 0.08 in CD₃CN+CDCl₃, a lot of solid present:

δ²⁹Si, Null;

δ¹H(ppm), 8.18(mt), 6.49(mt), 2.92(all were weak and broadened);

δ¹⁹F, Null.

HSiCl₃, r = 6.3, c = 21 in CD₃CN+CDCl₃:

δ²⁹Si(ppm), -150.98(sh, J_{Si-H} 303.3 Hz);

δ¹H(ppm), 8.17(d), 8.12(d), 6.76(d), 6.69(d), 3.23, 2.94; 5.33.

SiCl₄, r = 7.0, c = 0.07 in CD₃CN+CDCl₃, a lot of solid present:

δ²⁹Si(ppm), -162.99;

δ¹H(ppm), 8.20(l, d), 8.18(s,d), 6.57(l, d), 6.55(s, d), 3.02(l), 3.26(s).

(III) Interactions of PhHSiCl₂ with r NMI (c = 0.4), solids formed at r=2 in CDCl₃ and at r=3 in CD₃CN:

	δ ²⁹ Si(ppm)	δ ¹ H(ppm)
r=1,	Null	7.69, 7.46(mt) 6.04; 8.88, 7.20, 6.96, 3.95(in CDCl ₃)
r=2,	Null	7.55, 7.40(mt), 6.12; 8.90, 7.24, 6.92, 3.96(in CDCl ₃)

	Null	7.56, 7.42(mt), 6.10; 8.68, 7.25, 7.11, 3.77(in CD ₃ CN)
r=3	Null	7.52(vbr), 5.54; 8.46, 7.24, 7.10, 3.77(in CD ₃ CN)

(IV) Interactions of PhSiCl₃ with r DMPU in CDCl₃(c = 0.6):

	$\delta^{29}\text{Si}(\text{ppm})$	$\delta^1\text{H}(\text{ppm})$
r=1,	-0.93	7.75, 7.56(mt) 3.24(t), 2.92, 1.95(qu)
r=6,	-0.71	7.75, 7.60(mt) 3.26(t), 2.92, 1.96(qu)
r=9,	-0.66	7.77, 7.62(mt) 3.26(t), 2.89, 1.96(qu)
	-2.42	7.78, 7.65(mt, br) 3.25(t), 2.91, 1.95(qu)(at 230 K).

7.5.2 Analyses of solid silane-nucleophile adducts

General procedure for solids isolation and analyses

Solid adducts of multifunctional silanes with nucleophiles were much more ready to deposit than those of monofunctional silanes. Some of the solids were made and analyzed. The silane was measured and transferred by a syringe in a solvent in a 25 or 50 ml reactor. An excess (usually up to six) equivalents of nucleophile was then injected slowly. In the case of DMAP, it was the silane that was injected into the DMAP solution. The mixture was then left to stay at least two days to let the particles grow. The solids were filtrated on a sintered glass and washed and dried with CHCl₃ or C₆H₁₄ at least three times under nitrogen and vacuum alternatively; and were finally dried under high vacuum at least five hours. The solids obtained were analyzed by elemental analyses and solution NMR if they could be re-dissolved.

Solids from NMI

Me₂SiCl₂·2 NMI: made from CH₂Cl₂; m.p 82~86°C;

Found C 40.70, H 6.50, N 19.57, Cl 25.03% (theoretically required C 40.95, H 6.19, N 19.10, Cl 24.18%);

NMR(δ , ppm; in CDCl_3):

^{29}Si , 11.7(sbr);

^1H , 8.27(2H, $\text{C}_3\text{-H}$), 7.14(4H, $\text{C}_{4,5}\text{-H}$), 3.81(6H, NMe),
0.96(6H, SiMe).

$\text{Me}_2\text{SiBr}_2 \cdot 2 \text{ NMI}$: made from CH_2Cl_2 ; m.p 168°C (sublimation);

Found C 31.28, H 4.95, N 14.83, Br 41.94% (theoretically
required C 31.43, H 4.75, N 14.66, Br 41.82%);

NMR(δ , ppm; in CDCl_3):

^{29}Si , Null(sbr);

^1H , 8.61(2H, $\text{C}_3\text{-H}$), 7.38(4H, $\text{C}_{4,5}\text{-H}$), 3.91(6H, NMe),
0.99(6H, SiMe).

$\text{Me}_2\text{SiI}_2 \cdot 3 \text{ NMI}$: made from CNCH_3 ; m.p $85\sim 152^\circ\text{C}$ (fusion);

Found C 29.01, H 4.88, N 14.11, I 48.01% (theoretically
required C 30.12, H 4.33, N 15.05, I 45.46%);

NMR(δ , ppm; in $\text{CD}_3\text{CN} + \text{CDCl}_3$):

^{29}Si , -32.3(sbr);

^1H , 8.57(3H, $\text{C}_3\text{-H}$), 7.32(6H, $\text{C}_{4,5}\text{-H}$), 3.91(9H, NMe),
1.36(6H, SiMe).

$\text{Me}_2\text{SiOTf}_2 \cdot 3 \text{ NMI}$: made from CH_2Cl_2 ; m.p $144\sim 150^\circ\text{C}$;

Found C 31.66, H 3.95, N 14.00, S 11.05% (theoretically
required C 31.89, H 4.01, N 13.95, S 10.64%);

NMR(δ , ppm; in CD_3CN):

^{29}Si , 45.4(sbr);

^1H , 8.21(3H, $\text{C}_3\text{-H}$), 7.30(d, 6H, $\text{C}_{4,5}\text{-H}$), 3.79(9H,
NMe), 1.14(6H, SiMe).

$\text{MeHSiCl}_2 \cdot 3 \text{ NMI} \cdot \text{CH}_3\text{CN}$: made from CH_3CN ; m.p $141.8 \pm 0.2^\circ\text{C}$;

Found C 45.41, H 6.20, N 25.47, Cl 16.64% (theoretically
required C 44.77, H 6.26, N 24.37, Cl 17.62%);

NMR(δ , ppm; in $\text{CD}_3\text{CN} + \text{CDCl}_3$):

^{29}Si , -169.5($J_{\text{Si-H}}$ 328 Hz);

^1H , 8.97(3H, $\text{C}_3\text{-H}$), 7.17(6H, $\text{C}_{4,5}\text{-H}$), 3.90(9H, NMe);

5.90(q, 1H, SiH), 1.37(d, 3H, SiMe);

0.85(3H, CH_3CN);

^{13}C , 138.6, 124.6, 122.0, 35.3(NMI);

116.8(sbr), 10.3(CH_3CN); 1.9(SiMe).

$\text{PhHSiCl}_2\cdot 3 \text{ NMI}\cdot \text{CDCl}_3$: made from CDCl_3 ; m.p $111.3 \pm 0.2^\circ\text{C}$;

Found C 40.32, H 4.67, N 15.75, Cl 31.96% (theoretically required C 41.97, H 4.82, N 15.45, Cl 32.60%);

NMR(δ , ppm; in $\text{CD}_3\text{CN} + \text{CDCl}_3$):

^{29}Si , -46.6(vbr, $J_{\text{Si-H}}$ 260 Hz);

^1H , 8.80(3H, $\text{C}_3\text{-H}$), 7.24(6H, $\text{C}_{4,5}\text{-H}$), 3.86(9H, NMe),

7.59, 7.40(mt, 5H, SiPh), 6.02(1H, SiH).

$\text{MeHSiOTf}_2\cdot 4 \text{ NMI}$: made from ($\text{CD}_3\text{CN} + \text{CDCl}_3$); m.p $136.3 \pm 0.5^\circ\text{C}$;

Found C 33.86, H 4.36, N 16.69, S 9.87% (theoretically required C 34.03, H 4.21, N 16.71, S 9.56%);

NMR(δ , ppm; in CD_3CN):

^{29}Si , -169.7($J_{\text{Si-H}}$ nr);

^1H , 8.14(4H, $\text{C}_3\text{-H}$), 7.20(d, 8H, $\text{C}_{4,5}\text{-H}$), 3.81(12H,

NMe); 5.80(1H, SiH), 1.21(3H, SiMe).

$\text{MeSiCl}_3\cdot 4 \text{ NMI}\cdot \text{CHCl}_3$: made from CHCl_3 ; m.p $169 \pm 0.1^\circ\text{C}$;

Found C 41.03, H 5.63, N 22.17, Cl 22.92% (theoretically required C 42.73, H 5.69, N 23.45, Cl 22.26%);

NMR(δ , ppm; in $\text{CD}_3\text{CN} + \text{CDCl}_3$):

^{29}Si , Null;

^1H , 8.53(4H, $\text{C}_3\text{-H}$), 7.17(d, 8H, $\text{C}_{4,5}\text{-H}$), 3.89(12H,

NMe); 7.55(1H, CHCl_3); 1.13(3H, SiMe).

PhSiCl₃·4 NMI·CH₂Cl₂: made from CH₂Cl₂; m.p 166±02 °C;

Found C 44.02, H 5.20, N 18.98, Cl 26.52% (theoretically required C 44.21, H 5.00, N 17.93, Cl 28.37%);

NMR(δ, ppm; in CD₃CN + CDCl₃):

²⁹Si, -175.2;

¹H, 8.20(4H, C₃-H), 7.08(8H, C_{4,5}-H), 3.74(12H, NMe);

8.10, 8.85(mt, 5H, SiPh); 5.42 (2H, CH₂Cl₂).

MeSiOTf₃·4 NMI: made from (CD₃CN + CDCl₃); m.p >350 °C;

Found C 29.30%, H 3.24, N 13.85, S 11.63% (theoretically required C 29.34, H 3.32, N 13.69, S 11.75%);

NMR(δ, ppm; in CD₃CN + CDCl₃):

²⁹Si, -169.5;

¹H, 8.95(4H, C₃-H), 7.11(8H, C_{4,5}-H), 3.89(12H, NMe),

1.31(3H, SiMe).

HSiCl₃·3 NMI: made from CHCl₃; m.p >250°C(decomposed);

Found C 37.78, H 5.27, N 20.58% (theoretically required C 37.75, H 5.02, N 22.01, Cl 27.86%);

NMR(δ, ppm; in CD₃CN + CDCl₃):

²⁹Si, -166.3(br, J_{Si-H} 327 Hz);

¹³C, 157.9, 139.1, 107.5, 40.3;

¹H, 8.01(d, 3H, C₃-H), 6.89(d, 6H, C_{4,5}-H), 3.22(d, 9H,

NMe); 0.53(mt, 1H, SiH).

HSiOTf₃·5 NMI: made from CHCl₃; m.p >190 °C(decomposed);

Found C 30.59, H 3.71, N 14.88, S 10.85% (theoretically required C 31.15, H 3.52, N 15.79, S 10.85%);

NMR(δ, ppm; in CD₃CN + CDCl₃):

²⁹Si, -186.2(J_{Si-H} 319 Hz);

^1H , 8.24(5H, $\text{C}_3\text{-H}$), 7.25(10H, $\text{C}_{4,5}\text{-H}$), 3.86(15H, NMe), 5.87(1H, SiH).

$\text{SiCl}_4 \cdot 3 \text{ NMI}$: made from CH_3CN ; m.p. $>195^\circ\text{C}$ (decomposed);
Found C 34.92, H 4.88, N 20.27, Cl 30.20% (theoretically required C 34.63, H 4.36, N 20.17, Cl 34.07%);
NMR(δ , ppm; in $\text{CD}_3\text{CN} + \text{CDCl}_3$):
 ^{29}Si , Null;
 ^1H , 8.08(3H, $\text{C}_3\text{-H}$), 6.72(6H, $\text{C}_{4,5}\text{-H}$), 3.21(9H, NMe).

Solids from DMAP

$\text{Me}_2\text{SiBr}_2 \cdot 2 \text{ DMAP}$: made from ($\text{CD}_3\text{CN} + \text{CDCl}_3$), m.p. $222\sim 237^\circ\text{C}$;
Found C 40.05, H 5.54, N 12.49, Br 35.75% (theoretically required C 41.57, H 5.67, N 12.12, Br 34.57%);
NMR was not run as the solid could not be re-dissolved.

$\text{Me}_2\text{SiOTf}_2 \cdot 2 \text{ DMAP}$: made from CHCl_3 , m.p. $144.4 \pm 0.1^\circ\text{C}$;
Found C 35.32, H 4.34, N 9.74, F 19.92, S 11.69%
(theoretically required C 36.00, H 4.36, N 9.36, F 18.98, S 10.68%);
NMR (δ ppm, in $\text{CD}_3\text{CN} + \text{CDCl}_3$):
 ^{29}Si , Null;
 ^1H , 8.07(d, 4H, $\text{C}_{2,6}\text{-H}$), 6.93(d, 4H, $\text{C}_{3,5}\text{-H}$), 3.19(12H, NMe); 1.21(6H, SiMe).

$\text{MeHSiCl}_2 \cdot 3 \text{ DMAP}$: made from CDCl_3 , m.p. $127 \pm 1^\circ\text{C}$;
Found C 52.44, H 7.22, N 16.94, Cl 16.74% (theoretically required C 54.87, H 7.12, N 17.45, Cl 14.72%);
NMR (δ ppm, in $\text{CD}_3\text{CN} + \text{CDCl}_3$):
 ^{29}Si , -83(sbr);

^1H , 8.09(d, 6H, $\text{C}_{2,6}\text{-H}$), 6.77(d, 6H, $\text{C}_{3,5}\text{-H}$), 3.19(18H, NMe); 5.45(sbr, 1H, SiH), 0.89(3H, SiMe).

$\text{MeSiCl}_3 \cdot 4 \text{ DMAP} \cdot \text{CDCl}_3$: made from ($\text{CD}_3\text{CN} + \text{CDCl}_3$), m.p. 153°C (sublimation);

Found C 46.19, H 5.84, N 14.45, Cl 25.01% (theoretically required C 47.50, H 5.97, N 14.77, Cl 28.04%);

NMR (δ ppm, in CD_3CN):

^{29}Si , Null

^1H , 8.08(d, 8H, $\text{C}_{2,6}\text{-H}$), 6.79(d, 8H, $\text{C}_{3,5}\text{-H}$), 3.16(24H, NMe); 1.19(3H, SiMe).

$\text{SiCl}_4 \cdot 2 \text{ DMAP}$: made from ($\text{CH}_3\text{CN} + \text{CHCl}_3$), m.p. $>226^\circ\text{C}$ (decomposed);

Found C 40.30, H 5.27, N 13.53, Cl 29.13% (theoretically required C 40.59, H 4.87, N 13.53, Br 34.23%);

NMR (δ ppm, in CD_3CN):

^{29}Si , Null;

^1H , 8.02(br, 4H, $\text{C}_{2,6}\text{-H}$), 6.74(br, 4H, $\text{C}_{3,5}\text{-H}$), 3.15(br, 12H, NMe).

Solids from DMF

$\text{Me}_2\text{SiBr}_2 \cdot 2 \text{ DMF}$: made from CH_3CN ; m.p. $122\sim 126^\circ\text{C}$;

Found C 26.44, H 5.60, N 7.67, Br 43.64% (theoretically required C 26.39, H 5.54, N 7.69, Br 43.88%);

NMR was not run as the solid could not be re-dissolved.

$\text{Me}_2\text{SiI}_2 \cdot 2 \text{ DMF}$: made from CH_3CN ; m.p. $93\sim 153^\circ\text{C}$ (fusion);

Found C 20.82, H 4.37, N 6.13, I 55.44% (theoretically required C 20.97, H 4.40, N 6.11, Br 55.40%)

NMR (δ ppm, in $\text{CD}_3\text{CN} + \text{CDCl}_3$):

^{29}Si , 20.0;

^1H , 8.96(2H, COH), 3.23, 3.46(12H, NMe);
1.12(6H, SiMe).

Solids from HMPA

$\text{Me}_2\text{SiOTf}_2 \cdot 2 \text{HMPA}$: made from CHCl_3 ; m.p. 85~92°C;

Found C 27.53, H 6.37, N 12.57, P 9.35, S 8.52% (theoretically
required C 26.89, H 5.92, N 11.76, P 8.67, S 8.97%);

NMR (δ ppm, in CD_3CN):

^{29}Si , -2.96

^1H , 2.81, 2.69(12H, HMPA); 0.79(6H, SiMe).

7.5.3 Conductivity studies of the mixtures of silanes and nucleophiles

General procedure

The production of ionic species in the interactions of silanes with nucleophiles was detected and measured by conductivity titrations with silanes against nucleophiles or vice versa in a specially designed conductivity cell under protection of nitrogen. About six millilitres of solvent, mainly CHCl_3 , CH_3CN or a mixture of them depending on the solubility of the silane nucleophile adducts under examination, was first put into the cleaned and dried conductivity cell. A silane or a nucleophile was then measured, weighed in the case of solids such as DMAP and uncertain specific gravity such as those of silyl triflates and SiCl_4 , and transferred into the cell by a syringe. Successive aliquots of the other reactant were then injected into the solution with stirring at a moderate speed. The conductivity of the mixtures was read and recorded after about one minute of every additions. The conductivity data against the molar ratios of nucleophile to silane or silane to nucleophile were summarized and illustrated in figures as listed below.

Figure 2.3: against Me_2SiCl_2 with NMI, DMF and HMPA;

Figure 2.7: against Me_2SiBr_2 with HMPA;

Figure 2.8: against Me_2SiBr_2 with NMI, DMAP and DMF;

Figure 2.11: against Me_2SiI_2 with NMI, DMF HMPA and DMPU;

Figure 2.16: against $\text{Me}_2\text{SiOTf}_2$ with NMI, DMF, DMPU and HMPA(Nu/Silane);

Figure 2.17: against $\text{Me}_2\text{SiOTf}_2$ with NMI, DMF, DMPU and HMPA(Silane/Nu);

Figure 2.21: against MePhSiCl_2 with NMI and HMPA;

Figure 2.24: against Ph_2SiCl_2 with NMI, DMF and HMPA;

Figure 2.25: against MeHSiCl_2 with NMI, DMF and DMAP;

Figure 2.27: against MeHSiCl_2 with DMPU and HMPA;

Figure 2.28: against RHSiOTf_2 with NMI;

Figure 2.29: against RHSiOTf_2 with DMPU and HMPA;

Figure 3.1: against MeSiCl_3 with NMI, DMF and DMAP;

Figure 3.2: against MeSiCl_3 with DMPU and HMPA;

Figure 3.3: against MeSiOTf_3 with NMI and DMF;

Figure 3.4: against MeSiOTf_3 with DMPU and HMPA;

Figure 3.5: against PhSiCl_3 with NMI and DMF;

Figure 3.6: against PhSiCl_3 with HMPA and DMPU;

Figure 3.7: against HSiCl_3 with NMI and DMF;

Figure 3.8: against HSiCl_3 with HMPA and DMPU;

Figure 4.1: against SiCl_4 with NMI and DMF;

Figure 4.2: against SiCl_4 with HMPA and DMPU.

7.6 Reactions of Si-H containing species

The reactions of Si-H containing species concern mainly the reduction reactions of unsaturated organic compounds. The primary studies were in a small scale, mostly carried out in 10 mm NMR tubes.

General procedure for the reduction of unsaturated organic compounds by Si-H containing species

The Si-H containing silane was first measured and mixed with about two millilitres

solvent, namely CDCl_3 , C_6D_6 or CD_3CN , in a 10 mm NMR tube. Then the additives were added quantitatively if they needed, including nucleophiles such as NMI, DMF and HMPA and salts such as Bu_4NOTf . The unsaturated organic compound was finally measured and transferred slowly into the mixture with shaking at room temperature or in an ice-bath. The NMR was run after half an hour and followed for a period of time if necessary.

Hydrolysis was carried out when the reduction reaction was found to have completed by NMR spectroscopy. Usually an adequate $\text{NaOH}/\text{H}_2\text{O}$ or $\text{CaHCO}_3/\text{H}_2\text{O}$ solution was added to the mixture in an ice-bath. The sample was left at least six hours for the hydrolysis to complete. There were two phases in cases CDCl_3 or C_6D_6 being the solvent. The organic phase was separated and further analyzed by NMR. In cases of CD_3CN being the solvent, diethyl ether was used to extract (at least three times) the organic products. The solvents were ultimately evaporated and the residues were analyzed by NMR spectroscopy.

Some of the NMR data of the reactions of Si-H containing species with unsaturated organic compounds are illustrated in Schemes of 6.1, 6.2, 6.3, 6.4, 6.6, 6.7 and 6.8 and Tables of 6.1 and 6.2. The additional information are presented in the tables below.

Table 7.2 NMR data of the reduction of aldehydes RCOH by Silanes Me_{3-n}HSiOTf_n

Silane (n=)	RCOH (R=)	Chemical shifts (ppm)		
		$\delta^{29}\text{Si}(\text{J}_{\text{Si-H}})$	$\delta^{13}\text{C}$	$\delta^1\text{H}$
2	Ph	-60.6(mt, sbr, J 8 Hz)	139.3(mt, s), 129.3(mt); 42.2(mt, l, CH ₂), 39.4(mt, CH ₂); -4.8(mt)	7.40, 7.27(br); 4.32, 3.98(l, br)(complex mixture); 0.78(l br)
1	Ph	1.2(7.8 Hz), -1.7(7,8 Hz)	139.4(mt, s), 129.3(mt); 41.9(mt, CH ₂), 39.2(mt, CH ₂), 35.9(mt, s, CH ₂); -0.23(mt), -0.4	7.11(br), 3.85(vbr) (complex mixture); 0.54(mt, l), 0.48
1	Me ₃ C	1.04(7.8Hz), -1.81(7.8Hz) *-19.2(6.8Hz), -21.6(mt)	83.93(CH ₂), 32.69(CH ₀), 26.66(CH ₃); -0.29, -0.46 *81.98, 32.40, 26.83; 1.72, 1.09, 0.80	3.33, 0.96(CH ₃); 0.54(mt, l), 0.48 *3.02, 0.91(ether); 0.08

* NMR data of the organic phases (CDCl₃) after hydrolysis with H₂O + CaHCO₃.

mt, means multiplet.

Table 7.3 NMR data of the reduction of ketones R^1R^2CO by $Me_3-nHSiOTf_n$ in $CDCl_3$.

R ¹	R ²	n	Chemical shifts (ppm)		
			²⁹ Si	¹³ C	¹ H
Ph	Me	2	-60.57(mt, J<10 Hz)	220~175(mt, s); 145~124(mt); 91.4(s); 49~44(mt, CH ₂); 42.9~37.3(mt, CH); 28.3~19.1(mt, CH ₃); -1.3~-5.3(mt)	8.45~7.20(mt); 5.04(mt); 4.1~3.0(mt), 2.16; 1.54~1.21; 0.66(mt)
Ph	Me	1	-1.8(mt, J<10 Hz); -18(mt, J<10 Hz)	216, 148~146(mt, s); 133~125(mt), 44(mt, CH); 29(mt, CH ₂); 24.6~15.9(mt); 0.8~-0.23(mt)	8.2~7.1(mt); 4.04(br, s), 3.01, 2.5(mt); 1.6~1.2(mt); 0.45(mt)
Ph	Ph	1	1.3(J=8.8Hz) H*-18.6~-21.4 (mt, J=6.8 Hz)	141.8, 129.5, 129.0, 126.7; 42.7(CH ₂); -0.3 H*141.0, 128.9, 128.4, 126.0; 41.9(CH ₂); 1.09~0.8(mt)	7.14; 3.87; 0.46 H*7.12; 3.87; 0.08
iBu	Me	1	4.1(J<5 Hz) H*-19~-22(mt, J≤6.8 Hz)	79.1(CH), 35.4, 25.6, 18.1; -1.4 H*75.5, 34.6, 25.5, 17.9; 1.1~0.5(mt)	3.76(q), 1.16(d, J 6.4Hz), 0.87; 0.47(mt) H*3.45(q), 2.46, 1.10(d, J 6.4Hz); 0.08
Me	Me	1	1.2, -1.7, -18; (J≤6.8 Hz)	74.1(80%), 68.4(CH); 25.6(s), 22.1; -0.23~-1.49(mt)	4.05(mt), 3.64(mt, s); 1.27(d, l), 1.13(d, s); 0.5(mt)

H* After hydrolysis with H₂O/CaCO₃.

Table 7.4 Summary of the reactions of PhCOR² with coordinated Si-H species

R ²	Complex & solvent	Time (h)	Chemical shifts (ppm)		
			$\delta^{29}\text{Si}/$ (J Hz)	$\delta^{13}\text{C}$	$\delta^1\text{H}$
Ph	[Me ₂ HSi-NMI ⁺]OTf ⁻ in CD ₃ CN	450	2.3/ (J 230)	140.1, 125.2, 124.3, 36.1(NMI ⁺); 197.0, 138.1, 133.3, 130.5, 129.1(Ph); -2.7	8.72, 7.80~7.34(mt), 3.93; 4.99(qu), 0.70(d)
H	[Me ₂ HSi-HMPA ⁺]OTf ⁻ in CDCl ₃	720	12.9/ (J 236)	192.6, 136.4, 134.7, 129.7, 129.1; 36.7, 36.4; -1.1	10.03; 7.85, 7.61(mt); 2.84, 2.73; 4.95(mt), 0.53(d)
H	[Me ₂ HSi-DMF ⁺]OTf ⁻ in CDCl ₃	96	3.8/ (J <8)	163.2, 41.2, 35.8(DMF ⁺); 138.4, 129.0, 128.4, 127.8; 72.2(CH ₂); -1.3	8.43, 3.41, 3.20(DMF ⁺); 7.38, 4.54; 0.57
H	[Me ₂ HSi ⁻ -NMI ⁺] ₂ OTf ⁻ in CDCl ₃	3	11.7/ (J 218)	137.4, 129.2, 121.6, 33.9(NMI), 137.4, 124.3, 119.7, 36.4(NMI ⁺); 134.9, 130.3, 129.2, 126.3, 85.0(CH); -2.0 *192.5, 136.7, 134.7, 129.8, 129.2	9.36, 7.87~7.07(mt), 3.96, 3.52; 4.72(sbr), 0.28(sbr) *9.97, 7.80~7.47(mt)
H	[MeHSi ⁻ OTf ₂ -HMPA ⁺] in CD ₃ CN	3	-56/ (mt, J <3)	141.8, 129.8, 127.6; 68.0(CH ₂); 36.9, 36.8; -5.2 *142.0, 128.5, 127.7, 126.8; 64.3(CH ₂)	7.38, 5.11; 2.76, 2.68; 0.82(mt) *7.26, 4.64
H	[MeHSi ²⁻ -NMI ⁺] ₄ OTf ⁻ ₂ in (CDCl ₃ + CD ₃ CN)	336	-169.9 /(J 346)	136.8, 124.6, 119.9, 36.7(s,NMI ⁺); 136.6, 125.7, 122.6, 34.5(NMI ⁺); 135.1, 130.9, 129.6, 126.3, 83.3(CH); 9.5 *192.6, 136.7 134.7, 129.8, 129.3	9.0, 8.07, 7.40, 7.13, 3.87(s), 3.74; 1.24 (all br) *10.01, 7.83~7.60(mt)

* After hydrolized with water and extracted with diethyl ether.

Table 7.5 Summary of the reactions of $\text{Me}_{3-n}\text{HSiOTf}_n$ with PhCOOH , MeCOOEt , HCONMe_2 and $\text{PhC}\equiv\text{CH}$ in solution.

Oxidizer	Reducing agent	solvent	Time (h)	Chemical shifts(ppm)		
				$\delta^{29}\text{Si}/$ (J Hz)	$\delta^{13}\text{C}$	$\delta^1\text{H}$
PhCO -OH	Me_2HSiOTf	CD_3CN + CDCl_3	21	23.2/ (J 239)	167.2, 134.8, 131.2, 130.5, 129.4; -1.2	13.1., 8.01(mt), 7.54 (mt); 4.96(mt), 0.57(d)
			680	13.8/ (J<7)	166.5, 135.1, 131.2, 129.5, 129.3; -0.6	8.09(mt), 7.55(mt); 0.78
MeCO -OEt	Me_2HSiOTf	CDCl_3	360	24.4/ (J 219)	171.1, 60.5, 21.0, 14.3; -1.5	4.10(q), 1.24(t), 2.01; 5.00(mt), 0.60(d)
HCO- NMe ₂	Me_2HSiOTf	CDCl_3	120	27.8/ (J 214)	163.6, 41.2, 36.0; -2.2	8.47, 3.47, 3.26; 5.05, 0.62(d)(all sbr)
PhC≡ CH	Me_2HSiOTf	CDCl_3	1168	24.2/ (J 221)	132.2, 129.4, 128.7, 125.5, 83.8, 78.0; -1.5	7.41(mt), 7.33(mt), 3.18; 4.87(mt), 0.56(d)
	MeHSiOTf_2	CD_3CN	120	-28.3/ (J 328)	132.5, 129.5, 129.1, 126.0, 83.8, 78.0; -0.5	7.43(mt), 7.35(mt), 3.31; 5.21(q), 0.91(d)
	MeHSiOTf_2 -3 NMI	CD_3CN	192	-131/ (vbr, J 305)	132.8, 129.9, 129.5, 84.2, 79.4(PhCCH); 139.3, 124.5, 124.0, 35.7(NMI ⁺); 6.6	7.41(mt), 7.33(mt), 3.51; 8.46, 7.31, 7.29, 3.82; 5.96(q), 1.23(d)

7.7 Sources of errors

Extensive precautions were taken to exclude moisture while handling moisture sensitive compounds, but the possibility of a very small percentage of hydrolysis cannot be entirely discounted.

A few synthesized silanes, such as MeHSiOTf_2 , PhHSiOTf_2 and HSiOTf_3 , contained a small amount impurities (2~10%), such as HOTf or other silanes. Therefore the measurements of quantity and molar ratios related to them is subject to uncertainty.

Weighings were done on a Sartorius digital balance with a accuracy of $\pm 0.01\text{g}$. The maximum deviation of the syringes from the indicated volume was determined by weighing measured volumes of distilled water and was found to be $\pm 0.7\%$.

Appendix 1 Summary of the properties of functional silanes

Silanes	b.p. (°C)	Chemical shifts (ppm)				
		S*	$\delta^{29}\text{Si}$	$J_{\text{Si-H}}(\text{Hz})$	$\delta^{13}\text{C}^{**}$	$\delta^1\text{H}$
Me_2SiHOTf	123	a	24.52	247	-1.55	5.01(mt), 0.59(d)
		c	25.41	234	-1.44	4.91(mt), 0.58(d)
Me_2SiCl_2	70	a	32.15		nr	0.8
		c	34.12			0.82
Me_2SiBr_2	112±1	a	19.86		9.59	1.10
		c	22.0			1.12
Me_2SiI_2	162±1	a	-33.96		12.58	1.58
		b	-32.31		12.70	1.59
		c	-33.52		13.58	1.58
$\text{Me}_2\text{SiOTf}_2$	(87±2)/ (10.2± 0.3) mmHg	a	14.65		-1.15	0.86
		b	15.36			0.88
		c	16.84			0.88
MePhSiCl_2	205	a	18.65	6	133.4, 133.0, 131.6, 128.3, 5.51	7.66(mt), 7.48(mt), 1.01
Ph_2SiCl_2	305	a	5.92			
		b	6.03		134.1, 132.1, 131.8, 128.6	7.68(mt), 7.46(mt)
MeHSiCl_2	41	a	10.70	265	5.4	5.59(q), 0.86(d)
		b	11.44	282		5.59(q), 0.91(d)
		c	12.51			

PhHSiCl ₂	(65~66)/ 10mmHg	a	-2.31	299		7.71(mt), 7.50(mt), 5.96
MeHSiOTf ₂	(75±1)/ 5mmHg	a	-8.23	296	-1.90	5.32(q), 0.96(d)
		b	-13.99	328		5.27(q), 0.95(d)
		c	-26.06	353	-0.63	5.19(q), 0.93(d)
PhHSiOTf ₂	nr	a	-28.2	323	135.0, 134.2, 129.4, 128.5	7.35(mt), 7.64(mt), 5.69
MeSiCl ₃	66	a	12.23	7.8		1.13
MeSiOTf ₃	(87±1)/ (3.8±01) mmHg	a	-51.73		-3.91	1.21
		b	-55.48	10	-3.04	1.24
		c	-57.60			1.24
PhSiCl ₃	201	a	-0.88		133.0, 132.6, 131.4, 128.5	7.74(mt), 7.50(mt)
PhSiF ₃ ***	100±1	a	-72.83(q)		134.8, 133.6, 128.9, 128.6	7.69(mt), 7.47(mt)
HSiCl ₃	31~32	a	-9.79	358		
		b	-9.47	370		6.15
		c	-8.39	380		6.16
HSiOTf ₃	nr	a	-76.04	416		5.47
HSi(O- <i>i</i> Pr) ₃	72±1	a	-62.43	282	65.37, 25.51	4.32(q), 1.25, 1.18
Si(OEt) ₄	169	a	-81.74		59.23, 18.15	3.85(q), 1.24(t)
SiCl ₄	57	a	-18.93			
		b	-18.65			

* S, solvent; a = CDCl₃, b = CD₃CN + CDCl₃, c = CD₃CN.

** The ¹³C values of CF₃SO₃ are not quoted, which is a quartet ranged from 141 to 96 ppm.

*** δ¹⁹F = -141.6 ppm, J_{Si-F} = 268 Hz.

**Appendix 2 Summary of the physical properties of
solvents, nucleophiles and relative compounds**

Nu	β	pKa	DN	AN	ϵ	π^*	$\delta^{13}\text{C}$ (ppm)	$\delta^1\text{H}$ (ppm)
DMF	0.69		26.6	16.0	36.5	0.88	162.5, 36.3, 31.1	8.00, 2.98, 2.84
DMAP	0.87	9.61					154.1, 149.6, 106.5, 38.8	8.23(d), 8.17(d), 6.47(d), 6.41(d), 2.92
NMI	0.82	7.3					137.9, 129.0, 120.3, 33.0	7.37, 6.96, 6.85, 3.53
DMPU	0.79						156.5, 47.9, 35.4, 22.2	3.22(qu), 2.89, 1.88(t)
HMPA	1.05		38.8	10.6	30.0	0.87	36.8, 36.7	2.68, 2.59
CH ₃ CN	0.31		14.1	18.9	38.0	0.75	117.2, 1.8	1.99
CH ₂ Cl ₂	0.00			20.4		0.82	53.8	5.28
CHCl ₃	0.00			23.1	4.8	0.58	77.2	7.26
C ₆ H ₆	0.10		0.1	8.2	2.3	0.59	128.5	7.40
Et ₂ O	0.47		1.92	3.9	4.3	0.27	66.0, 15.4	3.45(q), 1.18(t)
PhCOOH	0.38						171.2, 134.0, 130.2, 129.7, 128.9	11.6, 8.14~7.46(mt)
Me ₂ CO	0.48		17.0	12.5	20.7	0.71	206.6, 30.4	2.15
Ph ₂ CO	0.44						196.4, 137.5, 132.4 129.8, 128.2	7.71(mt), 7.47(mt)
PhCOMe	0.49					0.88	197.9, 137.1, 133.0, 128.6, 128.3, 26.5	7.87(mt), 7.46(mt); 2.53
Me ₃ C- COMe	0.48						213.5, 44.3, 26.4, 24.6	2.14, 1.14

Nu	β	pKa	DN	AN	ϵ	π^*	$\delta^{13}\text{C}$ (ppm)	$\delta^1\text{H}$ (ppm)
Me ₃ C-COH							205.7, 42.4, 23.4	9.47, 1.07
PhCOH	0.44					0.92	192.2, 136.5, 134.3, 129.6, 129.0	9.95; 7.79, 7.44(mt)
PhCH ₂ -OH	0.50					0.98	140.9, 128.3, 127.2, 126.9, 64.3	7.24, 4.47
PhCH ₂ O-CH ₂ Ph	0.41					0.80	138.3, 128.3, 127.6, 127.5, 71.9	7.23, 4.42
(PhCH-Me) ₂ O							139.5, 129.0, 128.1, 128.0, 75.8	
PhCH-(OH)Me								7.21, 4.88(q), 1.50(d)
Ph ₂ CH ₂							141.3, 129.0, 128.5, 126.2, 42.1	7.21, 3.99
Me ₂ CHO-CHMe ₂	0.49					0.27	24.3, 69.2	3.66(mt), 1.19(d)
Me ₂ CH-OH	0.95			33.5		0.48	25.1, 63.4	4.06(mt), 1.21(d)
Me ₃ CCH-(OH)Me							74.8, 35.0, 25.5, 17.9	3.45(q), 1.16(d), 0.90
Me ₃ C-CH ₂ OH							72.6, 32.6, 26.3	3.30, 0.91

β , Taft's HBA basicity value; pKa, dissociation constant of bases in aqueous solution; DN, donor number; AN, acceptor number; ϵ , dielectric constant; π^* , index of dipolarity / polarizability; see also references 86, 87 and 88.

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